Probing the chemistry of CH₃I on Pt–Sn alloys

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Abstract

Adsorption and reaction of CH₃I (methyl iodide) on Pt(111) and the (2×2) and (√3×√3)R30° Sn/Pt(111) surface alloys was investigated primarily by using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). CH₃I adsorbs molecularly on Pt(111) at 100 K, and 34% of the adsorbed CH₃I monolayer decomposes during heating above 200 K in TPD. Competition occurs during heating within the chemisorbed layer between hydrogenation to produce methane and dehydrogenation that ultimately leads to adsorbed carbon. Alloying Sn into the Pt(111) surface decreases the heat of adsorption and the amount of decomposition of CH₃I. Alloyed Sn slightly reduces the CH₃I adsorption bond energy from 13.4 kcal/mol on Pt(111) to 11.4 kcal/mol on the (2×2) alloy with θSn 0.25 and 9.3 kcal/mol on the (√3×√3)R30° Sn/Pt(111) alloy with θSn 0.33. More notably, the Sn–Pt alloy surface strongly suppressed CH₃I decomposition. Only 4% of the adsorbed CH₃I decomposed on the (2×2) Sn/Pt(111) surface, and no decomposition of CH₃I occurred on the (√3×√3)R30° Sn/Pt(111) surface during TPD. Methane was the only hydrocarbon desorption product observed during TPD. These results point to the importance of adjacent “pure Pt” threefold hollow sites as reactive sites for CH₃I decomposition. Finally, we note that CH₃I, and presumably the other short-chain alkyl halides, are not reactive enough on Pt–Sn alloys to serve as convenient thermal precursors for preparing species small alkyl groups such as CH₃(a) for important basic studies of the reactivity and chemistry of alkyl groups on Pt–Sn alloys. Another approach is required such as the use of a CH₃-radical source or non-thermal activation of adsorbed precursors via photodissociation or electron-induced dissociation (EID).  
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1. Introduction

Generation of alkyl groups and studies of their reactivity on metal surfaces has been of interest for many years [1–11]. An understanding of this chemistry is important because of the role of these species as reaction intermediates in heterogeneous catalysis over metals [12,13]. The smallest alkyl group is methyl (CH₃) and a variety of techniques have been developed to prepare surface-bound methyl species on metal single crystals in UHV environments, including thermal activation of methane from molecular beams [14], CH₃⁺ ion beams [15], and thermal pyrolysis sources...
using azomethane as a precursor [16–18]. The most frequently used method involves the use of alkyl halides as precursors which can be thermally or photochemically activated on the surface to cleave the carbon-halogen bond [1–11]. For example, Zaera and co-workers have shown that adsorbed methyl groups can be prepared in this manner from CH₃I on Pt(111) above 200 K [4,5]. Subsequent thermal chemistry of the methyl groups involves a competition between hydrogenation and dehydrogenation resulting in desorbed methane and chemisorbed methylene, respectively, depending on the initial coverage on Pt(111) [4,5,19]. No C–C bond coupling of the adsorbed methyl groups on Pt(111) was observed [19].

Recently, we have shown that alloying Sn into a Pt(111) surface strongly affects the decomposition of several saturated and unsaturated hydrocarbons [20–25]. To extend these studies to include probing the chemistry of chemisorbed CH₃ groups, we report the investigation of methyl iodide adsorption and decomposition on two Sn/Pt(111) surface alloys. The (2×2) Sn/Pt(111) alloy thermally dissociates CH₃I to a small extent, helping to elucidate CH₃(α) and CH₂(α) reactions on this surface. However, CH₃I was reversibly adsorbed on the (p3/c2p3)R30° Sn/Pt(111) alloy with no decomposition during heating in TPD, so this approach is not reliable for probing the chemistry of CH₃(α) and other alkyl group on Pt–Sn alloys. HREELS was used, however, to identify the existence of adsorbed CH₃ groups on the (2×2) Sn/Pt(111) surface alloy.

2. Experimental methods

All experiments were performed in a two-level stainless steel UHV chamber with a base pressure of 8×10⁻¹¹ Torr as described elsewhere [26]. It was equipped with a four-grid, low energy electron diffraction (LEED) optics, double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), ion sputtering gun, UTI-100C quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD), HREELS spectrometer, and various metal and gas dosing facilities. The HREELS results shown herein were obtained later in a three-level UHV chamber with a base pressure of 2×10⁻¹⁰ Torr, as has been previously described [24]. The bottom level of this chamber contained an LK2000 spectrometer for HREELS.

The Pt(111) crystal was cleaned by repeated cycles of Ar⁺-ion sputtering and O₂ exposures at P₀₂ = 5×10⁻⁸ Torr with the crystal at 1100 K. The surface purity and long-range order were verified by AES and LEED, respectively. The crystal could be resistively heated to 1200 K and cooled to 90 K by using a liquid-nitrogen reservoir. The temperature was measured by a chromel–alumel thermocouple spot-welded directly to the crystal.

All TPD experiments were performed by heating at a constant rate of 4 K/s. The HREELS spectra were recorded in the specular scattering direction at an incident angle of 60° from the surface normal and incident electron beam energy of 1 eV. The overall energy resolution of the spectrometer was less than 6 meV (50 cm⁻¹) and the count rates at the elastic peak were 100 kHz for clean Pt(111). The spectra reported were normalized to the intensity of the elastic peak and taken with the sample held at a temperature of 100 K.

Methyl iodide (CH₃I) (Aldrich Chemical Company, 99.5% purity) was used as received. It was dosed onto the crystal through a Varian leak valve connected to a multichannel-array gas doser positioned directly in front of the crystal surface. The dose measurements reported here were not corrected for ion gauge sensitivity or any enhancement by the multichannel array doser.

Following the work of Paffett and Windham [27], the (2×2) Sn/Pt(111) and the (√3×√3)R30° Sn/Pt(111) ordered surface alloys were prepared by evaporating Sn onto the clean Pt(111) surface at 300 K and subsequently annealing the sample to 1000 K for 10 s. Depending upon the initial Sn coverage, the annealed surface exhibited a (2×2) or (√3×√3)R30° LEED pattern. These patterns arise from “surface alloys” that are formed which contain no second-layer Sn atoms [28]. The (2×2) structure has θₛₙ = 0.25 in the top layer and a 2D structure like the (111) face of the bulk Pt₃Sn crystal. The other is a substitutional alloy of composition Pt₃Sn with θₛₙ = 0.33 [21,28]. These
surfaces are quite “flat”, but there is an outward buckling of Sn above the Pt-surface plane of 0.20 Å [28]. The (2 × 2)-Sn/Pt(1 1 1) and the (√3 ×
√3)R30°-Sn/Pt(1 1 1) surface alloys will be referred to as the (2 × 2) and √3 alloys, respectively, for brevity in the rest of this paper.

3. Results and discussion

CH₃I adsorption was carried out on Pt(1 1 1) and both Sn/Pt(1 1 1) alloys at 100 K. The coverages used throughout this paper are referenced to the Pt(1 1 1) surface-atom density of 1.51 × 10¹⁵ atoms/cm² corresponding to θ = 1.0 ML. Adsorption and desorption kinetics were probed by TPD and surface reactions were investigated using TPD and HREELS. We will discuss the TPD results first, and then consider the findings in the HREELS experiments.

The main desorption products during TPD from Pt(1 1 1) were H₂, CH₄ and CH₃I. Fig. 1 shows the CH₃I TPD curves following different CH₃I exposures on Pt(1 1 1) at 100 K. H₂ and CH₄ desorption will be considered later, as shown in Figs. 2 and 3. Iodine also desorbs from Pt(1 1 1) as atoms in the 500–800 K temperature range, as observed by Henderson et al. [1]. C₂Hₓ and higher order hydrocarbons were monitored during our TPD, but they were not detected. These results for Pt(1 1 1) are consistent with previous studies [1,4,5].

Low coverages of CH₃I on Pt(1 1 1) were irreversibly adsorbed; i.e., no molecular CH₃I desorption occurs in TPD after exposures of 0.08 L or less. CH₃I desorption occurs with a peak at 256 K after a 0.16 L dose. This high temperature peak shifts lower to 233 K and a new peak appears at 133 K at higher coverages. The intensity of the low temperature peak continues to increase with higher exposures, and we associate this peak with desorption of a condensed multilayer film of methyl iodide on Pt(1 1 1). This low temperature peak at 133 K also exists on both alloys for CH₃I multilayers.

On the (2 × 2) alloy, a CH₃I desorption peak occurs at 220 K due to partially reversible adsorption even following low exposures of CH₃I,
as shown in Fig. 1. This peak shifts to 171 K near saturation of the monolayer. In contrast to the behavior on Pt(1 1 1), evolution of molecular CH$_3$I occurs in TPD even after the lowest exposure of
0.04 L (not shown). On the $\sqrt{3}$ alloy, CH$_3$I desorbs in a single, relatively narrow peak at 180 K at low coverages in the monolayer. This peak shifts to 168 K at monolayer saturation. On this alloy, there was completely reversible adsorption of CH$_3$I at any coverage and no desorption of other species was detected.

Coverage-dependent shifts in the CH$_3$I desorption peak from the monolayers shown in Fig. 1 are often explained by repulsive lateral interactions between adsorbates which decreases the activation energy for desorption with increasing initial coverage. Support for this explanation here comes from the work of Zaera and Hoffman [5] in which they found that CH$_3$I chemisorbs on Pt(111) with the C–I bond tilted with respect to the surface at low coverages, but reoriented to position the C–I bond perpendicular to the surface as the adsorbate coverage is increased.

The chemisorption bond energy of CH$_3$I is reduced on both of the Sn–Pt alloys compared to that on clean Pt(111). This reduction can be directly observed with TPD, because the adsorption energy is equal to the desorption activation energy, assuming a negligible activation energy for molecular adsorption which should easily be satisfied for this weakly bonded system. The CH$_3$I desorption peak at low exposures shifts from 256 K on Pt(111) to 220 and 180 K on the ($2\times2$) and $\sqrt{3}$ alloys, respectively. Thermal desorption activation energies, $E_d$, were estimated from the peak temperatures in the TPD curves that correspond to about 10% of the monolayer saturation coverage to minimize the influence of inter-molecular lateral interactions. By means of Redhead analysis [29], assuming first order desorption kinetics and a pre-exponential factor of $10^{11}$ s$^{-1}$ [30], we estimate that $E_d$ decreases from 13.4 kcal/mol on Pt(111) to 11.4 and 9.3 kcal/mol on the ($2\times2$) and $\sqrt{3}$ alloys, respectively. These values can also be compared to our estimate of $E_d$ for the sublimation energy of physisorbed CH$_3$I, condensed in the multilayer and desorbing near 133 K, of 8 kcal/mol assuming a pre-exponential factor of $10^{13}$ s$^{-1}$. Our result on Pt(111) is consistent with previous studies of CH$_3$I bond cleavage on Pt(111) that determined an $E_d$ value of 12.8 kcal/mol [31].

Partial decomposition of chemisorbed CH$_3$I also causes desorption of CH$_4$ and H$_2$ during TPD and leaves carbon on the surface. Fig. 2 compares the H$_2$ TPD traces for increasing CH$_3$I exposures on Pt(111) and the ($2\times2$) alloy. No desorption of H$_2$ occurred from the $\sqrt{3}$ alloy. On Pt(111), two main peaks occur, one at 333 K that shifts to 312 K at saturation, and another at 537 K that does not shift with increasing CH$_3$I exposures. This is consistent with previous reports in the literature [1,5]. The lower temperature peak, which is relatively large at low coverages, is likely to correspond to second-order kinetics due to H$_2$ desorption that is rate-limited by recombination of surface hydrogen adatoms. On the ($2\times2$) alloy, two H$_2$ TPD peaks occur at 386 and 543 K, and these do not increase much in size nor shift as the initial CH$_3$I coverage changes. It is worth mentioning that gas-phase H$_2$ does not dissociatively chemisorb on the ($2\times2$) alloy [32], and so there is no probability that the H$_2$ desorption observed from the alloy can originate from coadsorption of H$_2$ from the background gas.

Methane, CH$_4$, TPD traces following methyl iodide exposures on Pt(111) and the ($2\times2$) alloy at 100 K are presented in Fig. 3. No corresponding desorption of CH$_4$ was observed from the $\sqrt{3}$ alloy. On Pt(111), a CH$_4$ desorption peak at 274 K was seen at low coverages. This peak becomes broader and shifts to 294 K with a shoulder at 267 K at high initial CH$_3$I coverages. Zaera and Hoffmann [5] proposed that methane formation occurred by two different reaction paths that gave rise to two, reaction-rate limited CH$_4$ TPD peaks. Surface methyl groups formed by CH$_3$I decomposition are hydrogenated to methane by surface hydrogen which is available from background H$_2$ adsorption at low CH$_3$I coverages. However, surface hydrogen is mostly produced from partial dehydrogenation of methyl groups to form methylene at higher methyl iodide coverages, and this production of surface hydrogen controls the CH$_4$ formation and desorption kinetics.

CH$_4$ desorption from the ($2\times2$) alloy occurred in a peak fixed at 315 K for any coverage. The other peak at 220 K, which shifts to 186 K as the CH$_3$I exposure increases, is due to a cracking fraction from CH$_3$I molecular desorption. The
amount of CH₄ desorbed from the (2 × 2) alloy is much smaller (5% at saturation) than that from Pt(1 1 1), and the single 315-K peak is an indication that only one reaction path is important on this alloy under UHV conditions. This is consistent with observations that gas-phase H₂ dissociative chemisorption does not occur on this alloy surface [32], and thus H₂ adsorption from the background is eliminated. The 21-K shift to higher temperature in the CH₄ TPD peak upon alloying shows that activation energy for dehydrogenation of CH₃ to CH₂ groups increases on the (2 × 2) alloy, in an amount estimated to be about 2.2 kcal/mol over that on Pt(1 1 1).

The TPD data in Figs. 1–3 can be quantified to give “uptake plots” that reveal the CH₃I adsorption kinetics, as shown in Figs. 4 and 5. These plots also reveal the partitioning of adsorbed CH₃I into decomposition products (determined as TPD peak areas) for increasing amounts of methyl iodide adsorption on Pt(1 1 1) and both Sn/Pt(1 1 1) alloy surfaces. The saturation coverage for one monolayer of chemisorbed CH₃I on clean Pt(1 1 1) at 100 K in Fig. 4 was set to θₘono(CH₃I) = 0.20 ML, based on the results of Zaera and Hoffmann [5],

obtaining θ(CH₃I) = 0.132 ML in our case. The H₂ TPD peak area due to CH₃I decomposition was calibrated from ethylene decomposition after ethylene exposures on Pt(1 1 1) at 100 K and considering θ(CH₃I) = 0.25 ML and θ(CH₃I) = 0.11 ML, as reported in previous work [22,26]. According to
this estimate, and consistent with a constant value of the CH$_3$I sticking coefficient during formation of the monolayer, 33.5% of the CH$_3$I monolayer decomposes into CH$_4$ and H$_2$ during TPD, eventually leaving only carbon on the Pt(111) surface. This amount is lower than the 50% value found by Zaera and Hoffmann [5], and the 63% value of French and Harrison [9]. Possible explanations are that our crystal had fewer defects, or more likely, that we had better control of electron exposure from the ionizer region of the mass spectrometer in the current experiment than in previous work.

A comparison of the CH$_3$I TPD peak areas establishes that the coverage of chemisorbed CH$_3$I in the monolayer is the same on all three surfaces. On the (2×2) alloy, the amount of H$_2$ desorption was about 50% smaller than on Pt(111). Fig. 5 shows that the monolayer coverage of CH$_3$I on the (2×2) alloy at 100 K is $\theta_{\text{mono}}^\text{CH}_3\text{I} = 0.20$ ML, with $\theta_{\text{rev}}^\text{CH}_3\text{I} = 0.19$ ML and $\theta_{\text{dec}}^\text{CH}_3\text{I} = 0.01$ ML, i.e., 4% of the monolayer decomposes during TPD. On the $\sqrt{3}$ alloy, completely reversible adsorption of CH$_3$I occurs without any decomposition. These values are supported by the similar exposures required to form the monolayers on the three surfaces, which would be expected given a constant value of the CH$_3$I sticking coefficient on all three surfaces at 100 K.

Fig. 6 shows the vibrational spectrum of a CH$_3$I multilayer on the (2×2) alloy at 100 K. Energy loss peaks at 515, 895, 1254, 1435, 2970 and 3065 cm$^{-1}$ can be assigned to molecular CH$_3$I modes as $\nu$(C–I), $\rho$(CH$_3$), $\delta_s$(CH$_3$), $\delta_a$(CH$_3$), $\nu_s$(CH$_3$) and $\nu_a$(CH$_3$), respectively. Table 1 compares the energy loss peaks for the CH$_3$I multilayer spectrum in Fig. 6 to the vibrations in gaseous CH$_3$I [33] and previous studies of CH$_3$I adsorbed on Cu(111) [8] and Pt(111) by HREELS [1], and Pt(111) by IRAS [9].

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>CH$<em>3$I$</em>{ad}$ IR [33]</th>
<th>Cu(1 1 1) HREELS [8]</th>
<th>Pt(1 1 1) HREELS [1]</th>
<th>(2×2) Sn/Pt(1 1 1) HREELS [This work]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_a$(CH$_3$)</td>
<td>3060</td>
<td>3050</td>
<td>3045</td>
<td>3065</td>
</tr>
<tr>
<td>$\nu_s$(CH$_3$)</td>
<td>2969</td>
<td>2960</td>
<td>2970</td>
<td>2970</td>
</tr>
<tr>
<td>$\delta_s$(CH$_3$)</td>
<td>1438</td>
<td>1440</td>
<td>1405</td>
<td>1440</td>
</tr>
<tr>
<td>$\delta_a$(CH$_3$)</td>
<td>1251</td>
<td>1245</td>
<td>1230</td>
<td>1206, 1219</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>883</td>
<td>880</td>
<td>875</td>
<td>886, –</td>
</tr>
<tr>
<td>$\nu$(C–I)</td>
<td>533</td>
<td>535</td>
<td>480</td>
<td>515</td>
</tr>
<tr>
<td>$\nu$(M–I)</td>
<td></td>
<td></td>
<td>875</td>
<td>255</td>
</tr>
</tbody>
</table>
multilayer on the (2×2) alloy are not perturbed much from values determined by IR spectroscopy for CH$_3$I$_{(g)}$, as would be expected for a condensed, physisorbed film.

Heating the CH$_3$I multilayer on the (2×2) alloy from 100 to 130 K removes all physisorbed and multilayer species, but leaves most of the CH$_3$I adsorbed in the monolayer. Only small shifts occurred in the monolayer spectrum, but the relative intensities of the $\nu$(C–I), $\delta$(CH$_3$), and $\nu$(CH$_3$) peaks were increased. This indicates that the CH$_3$I molecule is still intact, but that the orientation of the C–I bond is more aligned with the surface normal compared to that in the multilayer film. However, the significant intensity of the $\delta$(CH$_3$) and $\nu$(CH$_3$) modes establishes that the C–I bond is not perpendicular to the surface. A small shoulder at 255 cm$^{-1}$ is also now detected and associated with the $\nu$(Pt–I) mode. We note that most of the broad loss feature from 500 to 900 cm$^{-1}$ centered at 707 cm$^{-1}$, and the loss peak near 1625 cm$^{-1}$ is due to co-adsorbed H$_2$O that accumulated at the surface during acquisition of the HREELS spectrum [8,34].

Henderson et al. [1] proposed that bonding of methyl iodide on Pt (111) occurs via the iodine atom. Later studies established that chemisorbed methyl iodide on Pt(111) adopts a tilted configuration (iodine atom down) at low coverages and an upright geometry with $C_{3v}$ symmetry at monolayer coverages [5]. Our results show that methyl iodide adsorbs on the (2×2) alloy near monolayer coverage quite similarly in a relatively upright configuration with the iodine atom next to the surface, but with the C–I bond tilted away from the surface normal. In addition, the vibrational frequencies of methyl iodide adsorbed in the monolayer on the (2×2) alloy are much closer to the physisorbed values than on Pt(111), which is consistent with a lower adsorption energy on the alloy.

Heating the adlayer on the (2×2) alloy to 200 K desorbs most of the CH$_3$I from the monolayer, but does not cause any H$_2$ or CH$_4$ desorption. This causes the vibrational spectrum to change, with peaks at 504, 865, 1143, 1390, 2963 and 3045 cm$^{-1}$. Some adsorbed CH$_3$I remains to contribute the peak at 1225 cm$^{-1}$ and we note again the unfortunate appearance of some features due to coadsorbed water in the spectrum. Based on the CH$_4$ evolution that eventually occurs in TPD from the alloy, and prior studies of CH$_3$I on Pt(111), we sought to establish evidence for the appearance of adsorbed methyl groups in our spectra. We must consider, however, that the concentration is expected to be only one percent of a monolayer or less. The vibrational mode assignments for some representative studies identifying adsorbed CH$_3$ groups are shown in Table 2. Comparisons to our spectrum obtained after heating to 200 K reveal a credible assignment of chemisorbed methyl groups on the (2×2) alloy with the observed new peaks corresponding to $\nu$(Pt–C), $\rho$(CH$_3$), $\delta$(CH$_3$), $\delta$(CH$_3$), $\nu$(CH$_3$) and $\nu$(CH$_3$) modes, respectively. The appearance of loss peaks from $\delta$(CH$_3$) and $\delta$(CH$_3$), along with $\nu$(CH$_3$) and $\delta$(CH$_3$), modes with similar intensities indicates that the methyl groups are chemisorbed with their $C_{3v}$ symmetry axis tilted away from the surface normal. This is

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**Table 2**

Vibrational frequencies of CH$_3$ ligands

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Bi(CH$<em>3$)$</em>{3(g)}$ [35]</th>
<th>Bi(CH$<em>3$)$</em>{3}$/Pt(111)</th>
<th>Cu(111)</th>
<th>Pt(111)</th>
<th>(2×2) Sn/Pt(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>3054</td>
<td>2920</td>
<td>2905</td>
<td>2925</td>
<td>3045</td>
</tr>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>2994</td>
<td>2971</td>
<td>2852</td>
<td>–</td>
<td>2963</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>1383</td>
<td>1388</td>
<td>1456</td>
<td>–</td>
<td>1390</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>1160</td>
<td>1140</td>
<td>1366</td>
<td>1220, 1224</td>
<td>1143</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>780</td>
<td>789</td>
<td>897</td>
<td>520</td>
<td>255</td>
</tr>
<tr>
<td>$\nu$(M–C) ($\nu$(Bi–C))</td>
<td>460</td>
<td>453</td>
<td>345</td>
<td>504</td>
<td></td>
</tr>
<tr>
<td>$\nu$(M–I)</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

46

similar to the geometry of methyl groups bound on Pt(111) [9,18].

As shown in Table 2, very close agreement exists between the vibrational frequencies of methyl groups chemisorbed on the (2 × 2) alloy and bound in molecular Bi(CH3)3 adsorbed on Pt(111) [35]. This agreement is better than the comparison to methyl groups bound on Pt(111). This is reasonable if, as expected, the methyl group is more weakly chemisorbed on the alloy than on Pt(111), and thus more closely resembles the chemical bonding between CH3 and Bi, a main group metal much less reactive than Pt.

As shown in the top curve following heating to 300 K, the trace amount of chemisorbed hydrocarbon fragments cause small loss peaks at 1041, 1191 and 1448 cm−1 which correspond to δ(CH) modes for these species, possibly a mixture of fragments such as CH in different configurations [36]. The peak at 255 cm−1 is due to the v(Pt–I) mode, and coadsorbed CO causes the loss peaks at 1865 and 2084 cm−1 [32]. The species that remain adsorbed on the alloy at 300 K are due to dehydrogenation and or condensation of methyl groups. Methylene (CH2) groups, observed by Zaera on Pt (111) under similar conditions [19], are likely intermediates in this chemistry, but CH2(a) vibrations are not consistent with the spectrum obtained from the alloy at 300 K.

Fig. 7 summarizes the influence of alloying Sn into the Pt(111) surface with regard to several parameters describing the adsorption, desorption and reaction of CH3I. Fig. 7 compares the amount of CH3I decomposition on Pt(111) and two alloys. Alloying the Pt(111) surface with Sn strongly suppresses CH3I decomposition, by an order of magnitude on the (2 × 2) alloy with θSn = 0.25 and completely on the √3 alloy with θSn = 0.33. We have previously pointed out that the absence of adjacent threefold “pure Pt” sites on the (2 × 2) alloy and the absence of any threefold “pure Pt” sites on the √3 alloy might play an important role in the low reactivity of these alloys. Such sites or “ensembles” would be expected to stabilize the transition state and the I(a) reaction product from CH3I decomposition. Alloying affects the CH3I adsorption energy to a smaller extent. These energies are equivalent to the thermal desorption activation energies Ed for CH3I on these surfaces. Values of Ed, as estimated by Redhead analysis [29], are given on the right hand side of Fig. 7. Removal of the threefold “pure Pt” sites on the √3 alloy appears to cause a much larger effect on the CH3I adsorption energy than would be expected simply based on the amount of Sn in the surface layer such as might be estimated based on the data from the (2 × 2) alloy. It is instructive to also compare all of these values to our estimated value of 8 kcal/mol for the sublimation energy of CH3I from the condensed multilayer.

The following elementary reaction steps can account for the H2 and CH4 products observed in TPD from the reaction of CH3I on the (2 × 2) Sn/ Pt(111) alloy:

\[
\text{CH}_3\text{I} \rightarrow \text{CH}_3(a) + \text{I}(a), \quad 130 < T < 200 \text{ K} \tag{1}
\]

\[
\text{CH}_3(a) \rightarrow \text{CH}_2(a) + \text{H}(a), \quad 200 < T < 300 \text{ K} \tag{2}
\]
\[
\text{CH}_3(a) + H(a) \rightarrow \text{CH}_4(g), \quad T > 270 \text{ K} \quad (T_p = 315 \text{ K}) \\
\text{CH}_2(a) + H(a) \rightarrow \text{CH}_4(g), \quad 200 < T < 300 \text{ K} \quad (T_p = 386 \text{ K}) \\
2H(a) \rightarrow \text{H}_2(g), \quad 340 < T < 500 \text{ K} \quad (T_p = 386 \text{ K}) \\
n\text{CH}(a) \rightarrow \text{C}_n(a) + nH(a), \quad T > 500 \text{ K} \quad (T_p = 543\text{ K}) \\
\]

The absence of \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) desorption, even though these molecules are reversibly adsorbed on the alloy, indicates that C–C bond coupling reactions such as the recombination of \( \text{CH}_3 \) groups are negligible under these conditions.

Low energy electron induced dissociation (EID) of multilayers of cyclohexane [23] and \( \text{C}_5-\text{C}_8 \) cycloalkanes [25] has been used previously to prepare cycloalkyl intermediates on Pt(111) and Sn/ Pt(111) surface alloys. Generally, cycloalkenes and \( \text{H}_2 \) are the main species desorbed after EID of multilayer cycloalkanes on Pt(111) and Sn/ Pt(111) alloy surfaces. In addition, benzene desorption also occurred after EID of multilayer \( \text{C}_6-\text{C}_8 \)-cycloalkane films on both Pt–Sn surface alloys. Thus, cycloalkyl dehydrogenation occurs extensively on both Sn/Pt(111) alloys, and hence, it is evident that \( \text{CH}_3\text{I} \) cannot be used reliably as a thermal precursor under UHV conditions to yield \( \text{CH}_3(a) \) on Pt–Sn alloys. A solution to preparing high coverages of chemisorbed \( \text{CH}_3 \) species on these alloys for study is to use a pyrolytic source of \( \text{CH}_3 \) radicals [17,18] and we have such studies currently underway in our laboratory. Other non-thermal methods, such as EID or photochemical activation of \( \text{CH}_3\text{I} \) could also be considered.

### 4. Conclusions

Two ordered Sn/Pt(111) surface alloys with \( \theta_{\text{Sn}} = 0.25 \) and 0.33 ML exhibit a lower adsorption energy and reactivity of methyl iodide (\( \text{CH}_3\text{I} \)) than the Pt(111) surface. Molecular binding energies are reduced to 11.4 kcal/mol on the \( 2 \times 2 \) alloy and 9.3 kcal/mol on the \( \sqrt{3} \) alloy from 13.4 kcal/mol on Pt(111). On Pt(111) at 100 K, one-third of the chemisorbed layer decomposes to form \( \text{CH}_4 \) and \( \text{H}_2 \) during TPD, leaving carbon on the surface. Alloying with Sn caused a large increase in the amount of reversibly adsorbed \( \text{CH}_3\text{I} \). The presence of 25% Sn atoms in the \( 2 \times 2 \) alloy surface layer suppressed the \( \text{CH}_3\text{I} \) decomposition to 4%. Only \( \text{CH}_4 \) and \( \text{H}_2 \) were detected during TPD and adsorbed methyl (\( \text{CH}_3 \)) groups were identified at 200 K. Completely reversible adsorption and desorption of \( \text{CH}_3\text{I} \) occurred on the \( \sqrt{3} \) alloy with \( \theta_{\text{Sn}} = 0.33 \) and no decomposition was observed. The absence of adjacent threefold “pure Pt” sites on the \( 2 \times 2 \) alloy and the absence of any threefold “pure Pt” sites on the \( \sqrt{3} \) alloy which may be required to stabilize the transition state or \( \text{I}(a) \) reaction product is consistent with these results and this might play an important role in the low reactivity of these alloys. This eliminates the use of \( \text{CH}_3\text{I} \), and presumably other alkyl halides, as a thermal precursors under UHV conditions to yield \( \text{CH}_3(a) \) and other hydrocarbon intermediates on Pt–Sn alloys.

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### References