

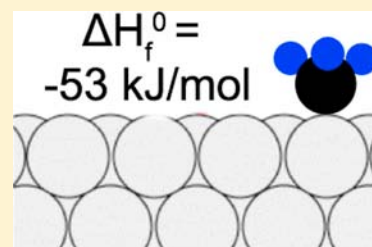
Energetics of Adsorbed CH₃ on Pt(111) by Calorimetry

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ABSTRACT: The enthalpy and sticking probability for the dissociative adsorption of methyl iodide were measured on Pt(111) at 320 K and at low coverages (up to 0.04 ML, where 1 ML is equal to one adsorbate molecule for every surface Pt atom) using single crystal adsorption calorimetry (SCAC). At this temperature and in this coverage range, methyl iodide produces adsorbed methyl (CH_{3,ad}) plus an iodine adatom (I_{ad}). Combining the heat of this reaction with reported energetics for I_{ad} gives the standard heat of formation of adsorbed methyl, ΔH_f⁰(CH_{3,ad}), to be −53 kJ/mol and a Pt(111)–CH₃ bond energy of 197 kJ/mol. (The error bar of ±20 kJ/mol for both values is limited by the reported heat of formation of I_{ad}.) This is the first direct measurement of these values for any alkyl fragment on any surface.



INTRODUCTION

The abundance of methane encourages discovery of new catalytic methods for processing this fuel. For this, it is important to understand the energetics of the adsorbed catalytic intermediates that result from its activation on late transition metal surfaces: −CH₃, −CH₂, and −CH. Platinum holds promise as an active catalyst ingredient for many of the reactions proposed for methane processing, and the Pt(111) surface is a prototype catalyst for the study of Pt and other Pt-group metals. Here, we report the first direct measurements for the energetics of adsorbed methyl on the Pt(111) surface or on any surface. We show that the calorimetrically measured Pt(111)–CH₃ bond energy of 197 kJ/mol differs by 64 kJ/mol from the value indirectly determined from temperature programmed desorption (TPD),^{1,2} but is very similar to DFT calculations using the PW91 and PBE functionals.^{3,4}

Previous TPD and RAIRS studies have shown that methyl iodide dissociates on Pt(111) to form CH_{3,ad} coadsorbed with I_{ad}. However, the further reduction of CH_{3,ad} to CH_{2,ad} and/or CH_{ad} also occurs, as does the production of methane and hydrogen gas.^{5–12} In this work, methyl iodide is dissociatively adsorbed on Pt(111) to form CH_{3,ad} coadsorbed with I_{ad} at low coverages (where no methane gas is produced), and the heat released in this coverage range is measured directly using single crystal adsorption calorimetry (SCAC). Since the energy of adsorbed iodine atoms has been determined already by careful TPD studies,¹³ we can extract from this heat the enthalpy of formation of CH_{3,ad}.

We report elsewhere our more extensive SCAC measurements of the energetics of the adsorption of methyl iodide on Pt(111), which covers the full coverage range up to saturation and temperatures in the range 95–320 K.¹⁴ There, we observed all of the following reaction steps:



and



as expected on the basis of prior literature.^{5–12} We further showed that, when the temperature is hot enough for reaction 2 to be fast enough to give accurate calorimetric heats, reactions 3 and 4 are also occurring so rapidly that they come to equilibrium. Since their net reaction equilibrium (i.e., CH_{3,ad} ⇌ CH_{ad} + 2 H_{ad}) is shown to lie far to the left, the combination of reactions 1 and 2 (i.e., CH₃I_g → CH_{3,ad} + I_{ad}) can be observed cleanly only at low coverage. At coverages above 0.04 ML, reaction 5 also becomes fast enough to force this equilibrium to the right and complicate interpretation of the heat measurements. We focus in this present report on the heat associated with that combination of reactions 1 plus 2 at the temperature of 320 K and low coverage where the heat data are most easily analyzed. In spite of the low coverage used (0.04 ML), we found no evidence for any significant contribution from defect sites at the lowest coverages studied (0.004 ML).

EXPERIMENTAL SECTION

The apparatus and experimental methods for single crystal adsorption calorimetry (SCAC) on Pt(111) at temperatures from 100 to 350 K has been previously published.^{15,16} Detailed experimental procedures for CH₃I on Pt(111) can be found in ref 14. Briefly, calorimetry was performed by exposing the Pt(111) surface to a pulsed molecular beam of methyl iodide (CH₃I) gas. Each pulse was 100 ms long, contained ~0.004 ML of CH₃I, and was repeated every 5 s. The methyl iodide (Fisher Scientific, 99.9%, lot 080482) was outgassed by several freeze–pump–thaw cycles after being put into its reservoir on the vacuum chamber. The reservoir was shielded from light to prevent

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photolysis. Its purity during use was checked with a mass spectrometer and found to be consistent with the manufacturer's claim. The beam was created by expanding ~ 2.0 mbar of CH_3I_g through a microchannel array at 299 ± 6 K (defining the gas temperature) and then collimated through a series of five liquid nitrogen cooled orifices as described previously.¹⁶

Sticking probabilities were measured simultaneously with calorimetric measurements, using the King and Wells method,¹⁷ whereby a mass spectrometer, without line-of-sight to the sample, measured the background pressure increase of CH_3I_g ($m/e = 142$) in the chamber vs time.

RESULTS

From previous TPD and RAIRS studies it is known that methyl iodide on Pt(111) undergoes C–I bond scission at temperatures greater than ~ 250 K to form high concentrations of methyl groups coadsorbed with iodine adatoms.^{5,6,11} However, these methyl groups can further dehydrogenate to $\text{CH}_{3,\text{ad}}$, evolving methane and hydrogen from the surface. In the experiment presented here, CH_3I_g is dosed onto a Pt(111) surface held at 320 K. At this temperature the kinetics of the C–I bond scission is found to be fast enough so that no broadening of the heat signal line shape is detected. This is an important condition to satisfy, since heat-signal analysis in SCAC is most reliable at conditions where the reaction is fast enough to occur within the 100-ms pulse of the molecular beam, so that no deconvolution of the heat signal is needed.¹⁸

The sticking probability of CH_3I_g on Pt(111) was measured in the coverage range from 0 to 0.04 ML of dissociatively adsorbed CH_3I and found to be 1.00 ± 0.01 . The corresponding heat of adsorption vs coverage is shown in Figure 1. The points here represent single gas pulses that are averaged over five identical calorimetry experiments. We observed no evolution of methane gas in this coverage range 0–0.04 ML. However, at higher coverages the evolution of methane gas was seen.¹⁴ Since the evolution of methane gas

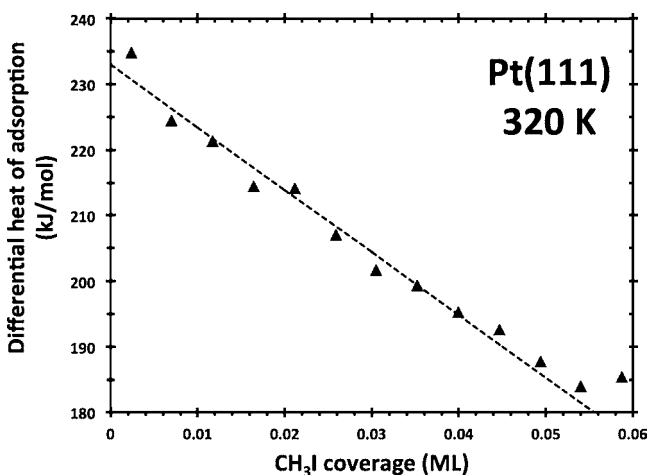


Figure 1. Differential heat of adsorption of CH_3I on Pt(111) at 320 K vs total coverage of dissociatively adsorbed CH_3I in the coverage range 0–0.06 ML. Each data point represents a pulse of ~ 0.004 ML of CH_3I gas and is the result of averaging five experimental runs. As discussed in the text, the heat of adsorption measured up to 0.04 ML represents the heat of dissociative adsorption on CH_3I_g to form $\text{CH}_{3,\text{ad}}$ coadsorbed with I_{ad} . The line shown is the best fit to the points below 0.045 ML and has a y-intercept of 233 kJ/mol and a slope of -953 kJ/mol/ML. One ML corresponds to 1.50×10^{15} dissociatively adsorbed CH_3I molecules per cm^2 .

indicates the methyl groups are further dehydrogenating to form $\text{CH}_{2,\text{ad}}$ and CH_{ad} (see above), we take the integral heat measured in the region 0–0.04 ML of 212 kJ/mol to represent the enthalpy of combining reactions 1 and 2 to give the net reaction:



Further evidence to support this assignment are reported in ref 14. Note in Figure 1 that the heat of reaction decreases smoothly with coverage, with no evidence of contributions from defect sites at the $\sim 1\%$ ML level that have significantly different heats. This is consistent with our other calorimetry results for Pt(111) surfaces prepared in the identical way, where if defects were present they showed increased heats only below 1% of a ML.^{18–20}

DISCUSSION

Energetics of Adsorbed Methyl. Using the measured enthalpy of reaction 6 of -212 kJ/mol a thermodynamic cycle is constructed in Figure 2 to extract the enthalpy of formation (ΔH_f^0) and Pt–C bond enthalpy for adsorbed methyl. The enthalpy of formation of adsorbed methyl is found by first starting on the left-hand side of the cycle with the elements in their standard states and following the pathway of the bottom half of the cycle. The enthalpy for the lower left-hand step is simply the enthalpy of formation of CH_3I_g , $+14.6$ kJ/mol, from ref 21. The lower right-hand step is our integral enthalpy of adsorption measured by SCAC at 320 K from 0 to 0.04 ML of coverage, -212 kJ/mol (Figure 1). By adding the enthalpies of the lower left- and right-hand steps, a total value of -197 kJ/mol is found. This is the total enthalpy change in taking the elements in their standard states to methyl coadsorbed with an iodine adatom (both at a coverage of 0.04 ML), and therefore is equal to the sum of the enthalpy of formation of adsorbed methyl with the enthalpy of formation of adsorbed iodine. The standard enthalpy of formation of iodine on Pt(111), $\Delta H_f^0(\text{I}_{\text{ad}})$, was estimated to be -144 ± 20 kJ/mol at 0.04 ML using the integral heat of adsorption of I_g at 0.04 ML of 251 ± 20 kJ/mol, estimated from the linear variation in the desorption energy of $\text{I}_{\text{ad}} \rightarrow \text{I}_g$ of $(255 - 199\theta) \pm 20$ kJ/mol reported in the TPD work of Labayen et al.¹³ We also used here the standard enthalpy of formation of I_g (107 kJ/mol²²). Subtracting $\Delta H_f^0(\text{I}_{\text{ad}})$ from -197 kJ/mol results in the enthalpy of formation of adsorbed methyl; $\Delta H_f^0(\text{CH}_{3,\text{ad}}) = -53$ kJ/mol. The maximum potential error on both values is ± 20 kJ/mol, based on the dominant error of ± 20 kJ/mol (on the heat of formation of I_{ad}).¹³

By following the pathway depicted in the upper part of this thermodynamic cycle (Figure 2) the C–Pt(111) bond enthalpy of adsorbed methyl can be extracted. This is accomplished by again starting on the left-hand side of the cycle with the elements in their standard states, but now following the upper left-hand step that takes the elements in their standard states to gas-phase methyl radical and adsorbed iodine. The enthalpy for this step is determined by adding the known enthalpy of formation of gas-phase methyl ($+147$ kJ/mol)²³ and adsorbed iodine (-144 kJ/mol at 0.04 ML),¹³ giving an enthalpy for this step of $+3$ kJ/mol. The upper right-hand step in the pathway is the adsorption of gas-phase methyl onto the Pt(111) surface that has 0.04 ML of adsorbed iodine. The enthalpy for this step is found by subtracting the upper left-hand step from -197 kJ/mol, giving an enthalpy of -200 kJ/mol (where the decimal

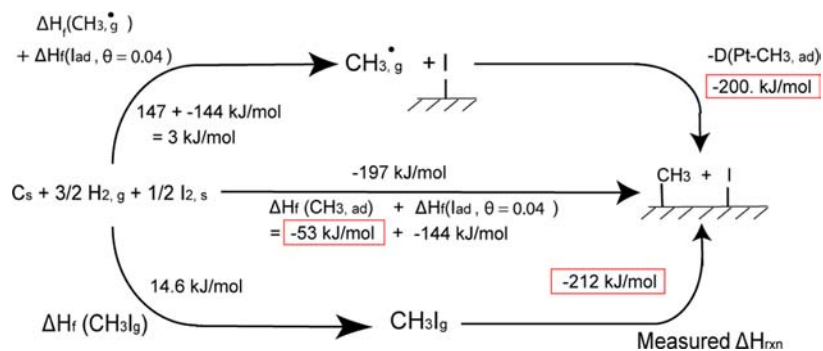


Figure 2. Thermodynamic cycle used in calculating the bond enthalpy and heat of formation of adsorbed methyl to the Pt(111) surface. Here, -212 kJ/mol is the integral enthalpy of reaction for $\text{CH}_3\text{I} \rightarrow \text{CH}_{3,\text{ad}} + \text{I}_{\text{ad}}$ measured at 320 K in region 1 (i.e., for methyl and iodide coverages of 0.04 ML).

here indicates significance to the last digit). Thus, the H_3C –Pt(111) bond enthalpy is 200. kJ/mol based on our heat measurement in the coverage range 0–0.04 ML at 320 K and other known thermodynamic data. Again, the maximum potential error is ± 20 kJ/mol. We note that the coadsorption of iodine does not perturb the activation energies for reactions of the methyl groups in any significant way,¹⁰ which suggests that these energetics measured here are not influenced by the presence of the low coverage of I_{ad} present here. Further evidence comes from RAIRS data that show that the band frequencies of adsorbed methyl produced through CH_3I dissociation are identical to those obtained by azomethane pyrolysis (which produces adsorbed methyl groups without the coadsorption of iodine).^{11,24}

Comparison to DFT. The energetics of adsorbed methyl measured by SCAC in this work provide benchmarks for comparison to DFT calculations of methyl on Pt(111). Table 1

Table 1. Comparison of the Measured Bond Energy of Adsorbed Methyl on Pt(111) to Calculated Bond Energies from Various DFT Methods^a

species	functional	coverage or cluster size	bond energy (kJ/mol)	ref
$\text{CH}_{3,\text{ad}}$ (atop)	current experiment	0.04 ML with 0.04 ML I_{ad}	197	this paper
	B3LYP	35 atom cluster	209	25
	B3LYP	10 Pt atom cluster	209	26
	PW91	10 Pt atom cluster	232	26
	B3LYP	8 Pt atom cluster	225	27
	PW91	1/4 ML	197	3
	RPBE	1/4 ML	163	3
	PBE	1/9 ML	192	4

^aWhen coverage is given, it refers to DFT with periodic boundary conditions, where the unit cell size defines the coverage.

lists the measured bond energy of adsorbed methyl, 197 kJ/mol, measured in this work (found by subtracting RT from the methyl bond enthalpy found in Figure 2) and also lists several calculated bond energies from various DFT methods. Here we find that cluster methods that use B3LYP calculate H_3C –Pt bond energies that decrease in energy (from 225 to 209 kJ/mol) with increasing cluster size, thus approaching our measured value as cluster size increases. The 10 Pt atom cluster calculation that uses the PW91 functional finds a bond energy that is 35 kJ/mol greater than what we measure. The periodic calculation using the PW91 functional for methyl on

Pt(111) at 1/4 ML of coverage finds a H_3C –Pt bond energy of 197 kJ/mol, in perfect agreement with our measured value. The periodic calculation using the PBE functional also performs well, calculating a bond energy of 192 kJ/mol at 1/9 ML of coverage, only 5 kJ/mol less than what we measure. Finally, the periodic calculation that uses the RPBE functional finds a much weaker H_3C –Pt bond energy of 163 kJ/mol, 34 kJ/mol less than the measured value.

Comparison to Results from TPD. It is also of interest to compare the measured energetics of adsorbed methyl from SCAC in this work to results from previous TPD and molecular beam studies. Zaera^{1,2} estimated the enthalpy for the dissociative adsorption of methane on Pt(111):



to be +50. kJ/mol, using the reported activation energy for dissociative adsorption of methane obtained from supersonic molecular beam studies (121 kJ/mol²⁸) minus the activation energy they measured for the reverse of reaction 7 (71 kJ/mol). This reaction enthalpy of +50. kJ/mol implies that the H_3C –Pt(111) bond enthalpy is only 136 kJ/mol, which is 64 kJ/mol less than measured here by SCAC (200. kJ/mol) and much less than any DFT calculation predicts in Table 1. Using the standard enthalpy of formation of adsorbed methyl measured by SCAC here (-53 kJ/mol), along with literature values for ΔH_{f}^0 of $\text{CH}_{4,\text{g}}$ (-75 kJ/mol²²) and H_{ad} (-36 kJ/mol at low coverage²⁹) allow the reaction enthalpy for reaction 7 to be calculated for Pt(111). This gives -14 kJ/mol for reaction 7 by calorimetry, 64 kJ/mol less than Zaera's value, and exothermic instead of endothermic. If one uses for Zaera's analysis a newer value for the activation energy for reaction 7 of 63 kJ/mol recently reported by Donald and Harrison³⁰ based on more extensive molecular beam studies and their more detailed theoretical interpretation, one gets much better agreement. Using this 63 kJ/mol value together with Zaera's activation energy for the reverse of reaction 7 (71 kJ/mol, see above), one instead gets -8 kJ/mol for the enthalpy of reaction 7, now just 6 kJ/mol less exothermic than the calorimetric value.

CONCLUSIONS

Single crystal adsorption calorimetry of the dissociative adsorption of methyl iodide on Pt(111) at 320 K from 0 to 0.04 ML has yielded the first direct measurement of the energetics of adsorbed methyl on any surface, giving a H_3C –Pt(111) bond enthalpy of 200. kJ/mol and a $\Delta H_{\text{f}}^0(\text{CH}_{3,\text{ad}})$ of -53 kJ/mol. Periodic DFT calculations using the PW91 and PBE functionals find bond energies very close to what we

measure here with SCAC, but previously reported energetics of methyl on Pt(111) determined indirectly from TPD studies differ by 64 kJ/mol.

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Notes

The authors declare no competing financial interest.

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