



Metal–carbon bond energies for adsorbed hydrocarbons from calorimetric data

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Abstract

Single crystal adsorption calorimetry (SCAC) is a powerful new method for measuring adsorption and reaction energies. Particularly for hydrocarbons, where little or no information is available from either experiment or theory on well-defined surfaces, this method can provide crucially needed information. Assignment of the measured calorimetric heats to the appropriate surface reaction yields directly reaction heats and heats of formation of surface species. An important extension using these results is to derive values for metal–carbon bond energies in adsorbed hydrocarbon species. In this paper we review the definition of the bond dissociation energy for a surface species and discuss methodologies and limitations for calculating accurate values of this quantity from measured calorimetric data. As a step in establishing benchmark data for adsorbed hydrocarbons, we calculate a Pt–C σ bond strength, $\langle D(\text{Pt}-\text{C}) \rangle$, of about 245 kJ/mol from data for ethylidyne on Pt{111}. Two independent methods, the quasiempirical valence bond (QVB) method and an average bond energy (ABE) method, were used to obtain this value, and the two values derived from these two approaches agree quite well. We also discuss the implications and applicability of this value of $D(\text{Pt}-\text{C})$ for other adsorbed hydrocarbons and on other Pt surfaces, and estimates of how this bond energy should differ when the C atom's ligands are different.

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Keywords: Single crystal surfaces; Chemisorption; Platinum; Carbon; Alkenes; Alkynes; Metallic surfaces

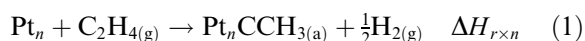
1. Introduction

The adsorption and decomposition of ethylene and acetylene on Pt, Rh, Pd, and Ni single crystal surfaces has recently been studied [1–7] using the single crystal adsorption calorimeter (SCAC) developed in Cambridge [8–10]. The work up to

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2000 has been reviewed [11,12]. Both the heat of reaction and the sticking probabilities are measured simultaneously as a function of coverage during the experiment. An assignment of the measured heat curves to a particular surface reaction provides a unique source of information on reaction heats and the heats of formation of surface species [11–21]. Pertinent to our present considerations, we take as an example the measurement by microcalorimetry [17] of the reaction enthalpy for the well-known conversion of gaseous ethylene to adsorbed ethylidyne



which includes the endothermic desorption energy of the initial hydrogen adatom product from the Pt surface (40 kJ/mol, from the isosteric heat of H_2 adsorption [22]). Reaction (1)'s energy leads directly to the standard heat of formation of adsorbed ethylidyne as

$$\Delta H_f^\ominus(\text{Pt}_n\text{CCH}_3(\text{a})) = \Delta H_{r \times n} + \Delta H_f^\ominus(\text{C}_2\text{H}_4(\text{g})) \quad (2)$$

These heats of formation can be used in a wide variety of thermochemical calculations for hydrocarbon reactions on surfaces, and have particular value as benchmarks for comparisons with theoretical calculations. Currently, SCAC provides the only direct experimental access to these heats of formation for adsorbed hydrocarbon fragments and many other adsorbed molecules [11,12]. For comparison, Ge and King [23] have conducted a full density functional theory slab computational analysis for the chemisorption and dissociation of ethylene on $\text{Pt}\{111\}$.

The metal–carbon bond strength is a fundamental quantity that can be used to gain some understanding of surface reactivity. It would also be useful in thermochemical calculations for surfaces. However, the determination of metal–carbon bond strengths from experimental data requires clear definitions of bond dissociation energies and a careful consideration of all the energy changes that occur at the surface due to adsorption. Two different approaches, which we specify as (i) the quasiempirical valence bond (QVB) method and (ii) the average bond energy (ABE) method, can be used in general to determine an average M–C bond energy. The value de-

rived depends on the method used, and for this reason it is desirable to outline here the advantages and limitations of both approaches.

2. Adsorbate–surface bond dissociation energy (BDE)

Bond dissociation energies are defined in relation to molecular potential energy curves that describe the bound and infinitely separated species. This is true at surfaces as with any other phases. Fig. 1. shows a potential energy diagram that can be used to discuss the Pt–ethylidyne bond dissociation energy, $D(\text{Pt}_n\text{–CCH}_3)$, which is the energy required for breaking the Pt–ethylidyne chemisorption bond at the Pt solid/vacuum inter-

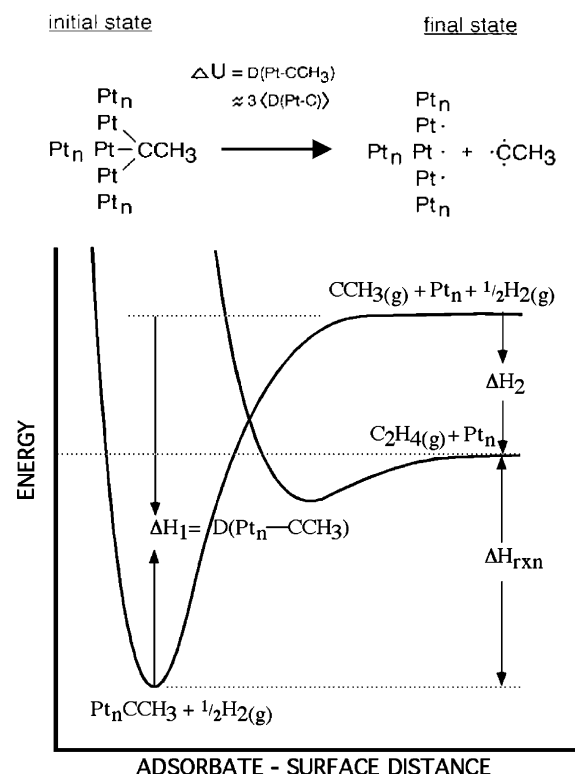


Fig. 1. Sketch of the potential energy curves that describe the platinum–ethylidyne bond dissociation energy, $D(\text{Pt}_n\text{–CCH}_3)$. An average value for the Pt–C single bond dissociation energy, $\langle D(\text{Pt–C}) \rangle$, can be obtained by taking 1/3 of the value of $D(\text{Pt}_n\text{–CCH}_3)$, because 3 σ bonds with the surface are broken.

face. This is defined as the energy difference between initial and final states, where the initial state is adsorbed CCH_3 , including the adsorbate-induced modification of the Pt atoms near the adsorption site and the metal-induced modification of the CCH_3 radical, and the final state is the Pt surface and the gas phase, free CCH_3 radical. Two alternative definitions of the final state are discussed below. We also show in Fig. 1 potential energy curves describing ethylene adsorption to make ethylidyne via reaction (1). Measurement of $\Delta H_{r \times n}$ for this reaction establishes the energy of $\text{CCH}_{3(a)}$ and thus enables a calculation to be made of $D(\text{Pt}_n\text{-CCH}_3)$. In this diagram, we highlight two other considerations explicitly. First, measurement of $\Delta H_{r \times n}$ in any practical experiment necessarily includes an additional contribution that is due to the adsorption-induced changes (e.g. weakening) in the Pt–Pt bonding at the surface. The implication is that this value of $\Delta H_{r \times n}$ includes the relaxation energy of the surface atoms, $\Delta H_r(\text{Pt}_n)$. It should also be added that the energy of any gaseous product must be considered, as shown in the reaction of O_2 with preadsorbed CO on Pt{110}, where the product CO_2 carries away an excess energy of about 50 kJ/mol [16].

There are two equally correct but different ways to define the bond dissociation energy (BDE): the diabatic bond dissociation energy and the adiabatic bond dissociation energy. The difference in these two values has to do with the final state of the gaseous and surface products. No problems arise in experiments or tables containing either of these values because there is no ambiguity in relating the two values: for the adiabatic bond dissociation energy the final state is the ground electronic state of all the products, while for the diabatic bond dissociation energy the final state is with the products in the electronic state corresponding to their electronic states (in terms of the intramolecular bonding) in their initial state. Either way of reporting bond dissociation energies will work as long as the initial and final states are defined. In almost all experiments, from gas phase chemical physics to inorganic and organic condensed phase reactions, one observes the thermalized or ground state product of the dissociation reaction and the

adiabatic bond dissociation energy is the one measured and reported.

For the ethylidyne– Pt_n surface bond, we can report either the diabatic bond dissociation energy or the adiabatic bond dissociation energy. The adiabatic bond dissociation energy refers to the gas phase ethylidyne product in its lowest energy electronic state (^2E) with only one unpaired electron and the fully relaxed clean Pt surface. The diabatic bond dissociation energy refers to the ethylidyne product in an electronic state (^4E) with three unpaired electrons, which is the electronic state that correlates to the adsorbed species (because the carbyne carbon in ethylidyne on Pt{111} is sp^3 -hybridized and forms three covalent bonds to the surface Pt atoms), and with the Pt surface in the identical configuration to that in the adsorption complex present, i.e., in the unrelaxed state. Both definitions of BDE are equally valid and differ numerically by the excitation energy of the gas phase product (i.e., the ^2E – ^4E energy gap in gaseous ethylidyne, $E_{\text{ex}}(\text{CCH}_3)$) and the relaxation energy of the Pt surface atoms, $\Delta H_r(\text{Pt}_n)$:

$$\Delta D = \Delta E_{\text{ex}}(\text{CCH}_3) + \Delta H_r(\text{Pt}_n) \quad (3)$$

We will come to a key point in the next section, that is, while there are two equally valid $D(\text{Pt}_n\text{-CCH}_3)$ values, we ultimately would like to derive an estimate for the Pt–C single bond energy from the calorimetry measurements. The diabatic BDE is more generally applicable but, as we will show, the adiabatic BDE is far simpler to use and gives good results when used in a way that recognizes its limitations.

The importance of clarifying this distinction when estimating metal–carbon bond energies is easily seen for a worst case scenario, formaldehyde ($\text{H}_2\text{C=O}$). The adiabatic bond dissociation energies are measured by experiment to be 368 and 67 kJ/mol, respectively, for dissociating the first H to make formyl radical and dissociating the second H to make CO. The C–H bond in formyl radical is very weak because of the enormous stabilisation energy gained in the fully-relaxed CO product [24]. Thus, while the adiabatic bond dissociation energy in formyl radical, $D(\text{H-C=O}) = 67 \text{ kJ/mol}$, is a valid number and is in fact what is measured, it is a terrible “predictor”

of C–H bond energies. However, taking the diabatic bond dissociation energy of formyl radical (forming CO in the final state in the triplet electronic state that corresponds to the intramolecular bonding in formyl radical in the initial state) gives a value closer to that expected for a typical C–H bond dissociation energy [24]. (One must compare this to a typical C–H bond energy for sp-hybridized C atoms, since HCO is nearly linear and so its C atom is nearly sp-hybridized.) This is then the basis of the QVB approach for predicting the C–H bond strength in such molecules if one breaks several bonds sequentially, to be described below.

Thus, a determination of the Pt–C single bond energy from measurements of the energy to form adsorbed ethynylidyne requires a focus on the diabatic bond dissociation energy if one wishes to involve gaseous CCH₃ in the analysis. On Pt{111}, the carbyne carbon in adsorbed ethynylidyne is fully sp³-hybridized, with no measurable hyperconjugation. The bonding of ethynylidyne to the surface is via three covalent Pt–C σ bonds so that the diabatic $D(\text{Pt}_n\text{-CCH}_3)$ is $\sim 3D(\text{Pt-C})$, where $D(\text{Pt-C})$ is an average Pt–C bond dissociation energy for a single σ bond. As we will show, the ABE approach to determining this same BDE must avoid involving gaseous CCH₃.

Calculation of the diabatic $D(\text{Pt}_n\text{-CCH}_3)$ from an adiabatic experimental measurement requires knowledge of $\Delta H_r(\text{Pt}_n)$ and of $\Delta E_{\text{ex}}(\text{CCH}_3)$, from Eq. (3). Recent ab initio DFT calculations have shown that for the clean surface of Pt{111} the energy difference between the fully relaxed clean surface and the clean surface with Pt atoms in positions corresponding to the structure with a monolayer of ethylene, $\Delta H_r(\text{Pt}_n)$ is ~ 5 kJ/(mol Pt atoms) [23], while for the conversion of Pt{100}hex to Pt{100}(1 \times 1) the experimentally measured energy difference is 21 kJ/(mol Pt) [14] and so this term can only be neglected for metal surfaces that do not show large reconstructions of the clean surface. Because CCH₃ is a hydrocarbon radical and experiments measuring radicals are quite challenging, very little information exists on their excited states. Ab initio quantum chemical calculations of these open shell species can be performed in principle, but little has been done at present. Thus, one is forced to estimate this

value. Two approaches are described in the next sections.

3. The quasiempirical valence bond (QVB) method

A powerful approach for estimating heats of adsorption and adsorbate–surface bond strengths which involves the use of diabatic BDEs has been described by Carter and Koel [25,26] in their quasiempirical valence bond (QVB) approach to surface thermochemistry. A large number of heats of formations for important gas phase species have already been tabulated [25,26]. The essence of this method is to determine the appropriate local electronic state of the adsorbate when bonded to the metal surface, in a manner similar to the valence bond approach to molecular electronic structure. This leads naturally to a determination of adsorbate bond dissociation energies and heats of formation of adsorbates. This approach relies on new (and improving) accurate measurements and calculations of heats of formation and the electronic excitation energies, ΔE_{ex} , for these unsaturated hydrocarbon radicals. The procedure to estimate the heat of formation of an adsorbate is as follows: (1) determine the number and nature (covalent, ionic, or dative) of chemical bonds from the adsorbate to the surface; (2) obtain the heat of formation of the gaseous species in its ground electronic state; (3) calculate the heat of formation of the gaseous species in an electronic state that most closely resembles the local electronic state of that species adsorbed on the surface; and (4) use heats of adsorption or diabatic bond energies to predict the heat of formation of the adsorbed species by subtracting the adsorbate–surface bond energies from the gas phase heats of formation. Below, we illustrate how this method can be used in reverse to estimate of the Pt–C bond dissociation energy $D(\text{Pt-C})$ for a single σ bond from the microcalorimetry results for ethylene dissociation to form ethynylidyne.

The QVB method is used to estimate the heat of formation of adsorbed ethynylidyne from a combination of the heat of formation of the gas phase ethynylidyne radical in its ground state and the appropriate excitation energy, as shown in

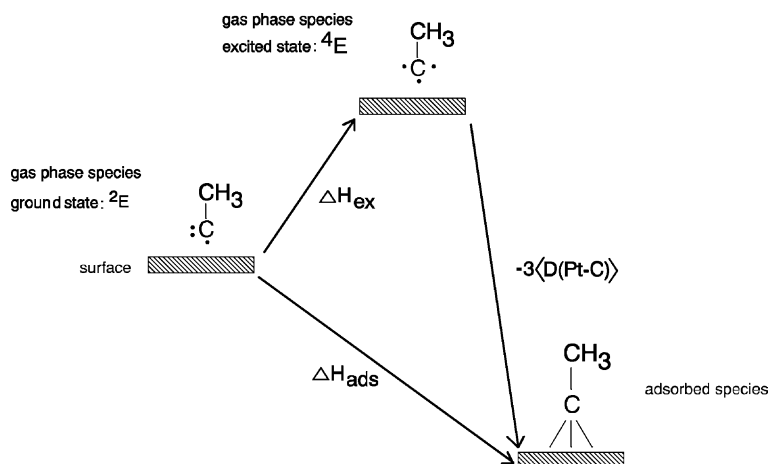


Fig. 2. Scheme for the thermochemical cycle required to calculate metal–carbon bond energies in the QVB methodology. As explained by Carter [25], excitation energies, ΔH_{ex} , to form the appropriate excited state must be used in conjunction with heats of formation data for the gas phase hydrocarbon radicals.

Fig. 2. In this method, $\Delta H_f(\cdot\ddot{\text{C}}\text{CH}_3, {}^4\text{E})$ can be calculated from the reaction



and is consequently given by

$$\Delta H_f(\cdot\dot{\text{C}}\text{CH}_3) = \Delta H_f(\cdot\ddot{\text{C}}\text{CH}_3) + \Delta E_{\text{ex}} \quad (5)$$

The difficulty in this method is that often, as here, the heats of formation and ΔE_{ex} are not known accurately and must be estimated. However, in most cases, these estimates have small error bars and so good values are obtained. Of course, these estimates can be continually improved as new experimental and theoretical results become available.

At this time, the best estimate of $\Delta H_f(\cdot\dot{\text{C}}\text{CH}_3)$ is (638.9 ± 14.6) kJ/mol as derived from $\Delta H_f(\cdot\ddot{\text{C}}\text{CH}_3) = 569.0 \pm 14.6$ kJ/mol and using for ΔE_{ex} the same ${}^4\text{E}-{}^2\text{E}$ splitting as in CH (69.9 kJ/mol) [26].

4. The average bond energy (ABE) method

In the second method, average bond energies and the principle of bond additivity can be used [27,28]. This methodology is a widely accepted

and powerful approach in inorganic and organic chemistry in predicting thermochemistry of gas phase species and reactions. All additivity rules to estimate molecular properties are based on the principle that “local” properties remain unchanged in a series of homologous compounds. The physical basis for this assumption is the fact that the forces between atoms in the same or different molecules are very short range. Based on these assumptions two different levels of accuracy can be discerned. In the first-order approximation partial values for the properties are assigned to different types of bonds in the molecule, thus distinguishing C–C from C=C, etc. The additivity of bond properties works within an error of ± 8 kJ/mol for the standard heats of formation of simple molecules; improvements are achieved when distinctions are made between different types of bonds, such as for example a C–C single bond next to a single or a double bond. A limitation is that it cannot be employed to distinguish differences in heats of formation of isomers. A further improvement can be made by assigning partial values of molecular properties to certain groups in the molecule and then summing up these group properties: the so-called second-order approximation [27]. This requires on the one hand two or more polyvalent (more than two ligand) atoms in the molecule

and on the other a very large data base for all the different possible groups. For increasing substitution the number of groups also increases. In this way the accuracy for the standard heat of formation of a simple molecule can be improved by a factor of four.

The level of approximation used in a given context depends on the information available. As a consequence, at the present time only the first-order approximation is applicable to adsorption and decomposition processes of hydrocarbons on single crystal surfaces observed by microcalorimetry.

In the application of the ABE method to surface science one can make important predictions that should be useful based on our current, extremely limited data base of metal–carbon bond energies. First, one recognizes that C–H and C–C bond energies are quite different at vinyl and carbonyl carbon atoms compared to sp^3 -hybridized carbon atoms. From the extensive tables of C–H and C–C bond dissociation energies (BDEs) of Benson [27] and McMillan and Golden [28], one can extract the approximate BDEs listed in Table 1. If M–C bonds follow the same trends as H–C or C–C bonds, one would expect M–C bonds at carbonyl carbons to be considerably weaker than M–C bonds at vinyl carbons.

A quantitative demonstration of this point has already been made with respect to metal–carbon bond energies in organometallic complexes, wherein several authors have shown that there is a linear correlation of slope 1.0 between metal–carbon bond strength and the corresponding hydrogen–carbon bond strength for the same ligand [29,30]. It has also been shown that this correlation extends to surface species on bismuth [30]. Fortunately, H–C bond energies are already thor-

oughly tabulated for a whole series of groups [28]. Some important values are listed in Table 2. The above mentioned 1:1 correspondence between these H–C bond energies and M–C bond energies gives predictability for many species provided that $D(M-C)$ for any one such group is available. This may be used to advantage by surface chemists, provided that experimental data on metal–carbon bond strengths is forthcoming for several different species adsorbed on a transition metal so that this correlation can be verified. This should be possible from microcalorimetry. Still, it should be recognized that the ABE method only predicts those contributions to the adsorption energy of this group that are provided by that specific two-center bond. Any additional bonding from other parts of the attached group, for example through π interactions or agostic bonding by other parts of the organic adsorbate at other sites on the metal surface, are ignored.

The ABE method is not intended to be applied to estimate reaction energies whenever multiple bond breaking occurs to form final products like gaseous carbene or ethylidyne. The bond strengths and heats of reaction predicted by the ABE method for such “spin impure” reactions often deviate strongly from the adiabatic measurements. For example, while the adiabatic dissociation energy to break the *first* C–H bond in formaldehyde (368 kJ/mol) in the example discussed earlier would be accurately predicted using the ABE for C–H bonds at carbonyl carbons from Tables 1 or 2 (364 kJ/mol), this ABE value would drastically overestimate the adiabatic dissociation energy to

Table 1
Approximate average bond dissociation energies (BDEs) as extracted from McMillan and Golden [28]

	H–C bond	C–C single bond
At carbonyl C	364	339
At normal secondary C	398	360
At normal primary C	410	360
At vinyl C (i.e., C=C)	460	423
At C≡C	552	526

All values are given in kJ/mol.

Table 2
Several H–C average bond energies, taken from values published by McMillan and Golden [28], in some cases averaged over similar ligands containing the same group

H–carbonyl	364
H–benzyl	368
H–i-C ₃ H ₇	398
H–ethyl	411
H–methyl	440
H–vinyl	460
H–phenyl	464
H–C≡C	552

All values are given in kJ/mol.

break the *second* C–H bond in formaldehyde (67 kJ/mol). Importantly, for the first C–H bond, 368 kJ/mol is both the adiabatic and diabatic bond dissociation energy since formyl radical has a doublet ground state.

Nonetheless, the extreme simplicity of the ABE method makes it very attractive, and one can often apply it to determine net reaction energies without involving species that require breaking a second bond on a radical, thus avoiding this “spin-impurity” problem. For example, consider the reaction whereby formaldehyde plus ethane are converted to acetone plus H₂:



While both C–H bonds in formaldehyde are “broken” and replaced with C–C bonds in this reaction, the ABE method nevertheless works quite well at estimating this reaction energy, which is calculated from the known heats of formation of the gaseous reactants and products [31] to be –25 kJ/mol. Using the ABE values from Table 1 for the C–H bond at carbonyl carbons (364 kJ/mol), the C–C bond at primary carbons (360 kJ/mol) and the C–C bond at carbonyl carbons (339 kJ/mol), along with the known H–H BDE (436 kJ/mol [31]), the reaction energy is estimated to be –26 kJ/mol by the ABE method, within 1 kJ/mol of the true value. One can think of each C–H bond replacement with a C–C bond as occurring sequentially when using the ABE method, rather than breaking both C–H bonds first. Thus, one can piece the steps together to achieve the net reaction while avoiding the “spin-impurity” problem mentioned above. As we will see below, this “spin-impurity” problem is also insignificant for the more complex case of ethylidyne on Pt considered here, because the net reactions actually measured do not have any reaction products in a non-zero spin state.

5. Results

5.1. Determination of $D(\text{Pt--C})$ for a Pt–C σ bond on Pt{111}

After introducing the QVB and the ABE methods as appropriate for determining average metal–

carbon bond energies from experimental calorimetric data, we now show a comparison of the application of each method to a particular system. A good example is the formation of CCH_{3(a)} + $\frac{1}{2}$ H_(g) on the Pt{111} surface from ethylene dissociative adsorption, reaction (1) [17]. As shown in Fig. 3, this reaction is assigned to take place at room temperature at an apparent coverage of 0.17 ML with a measured heat of reaction of –124 kJ/mol under conditions that the hydrogen atom produced from the reaction desorb as $\frac{1}{2}$ H_{2(g)} [17]. Calorimetry using SCAC establishes the heat of formation of ethylidyne on Pt{111} as –71.7 kJ/mol as calculated from Eq. (2) using $\Delta H_f^\ominus(\text{C}_2\text{H}_{4(g)}) = 52.3$ kJ/mol [26] as shown below:

$$\Delta H_{rxn} = \Delta H_f^\ominus(\text{CCH}_{3(a)}) - \Delta H_f^\ominus(\text{C}_2\text{H}_{4(g)}) \quad (7)$$

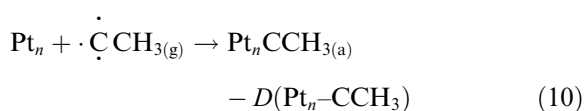
$$\Delta H_f^\ominus(\text{CCH}_{3(a)}) = (-124 + 52.3) \text{ kJ/mol} \quad (8)$$

$$= -71.7 \text{ kJ/mol} \quad (9)$$

When using calorimetric data in this way, one must recognize that the calorimeter measures only the energy associated with converting the pulse of gas into its final products, independent of how many transient adsorbed intermediates may be involved in reaching this final state. However, it must reach this final state within the time scale of the instrument response (typically 100–300 ms, depending on the calorimeter). Conversions that take slightly longer would cause a noticeable change in calorimeter signal lineshape. Conversions that are slower than the gas pulse repeat period (typically 1–2 s) would not contribute to the signal at all. For example, when ethylidyne is being produced in Fig. 3, the fact that it probably goes through a series of intermediates including di- σ ethylene does not impact the final measured energy or its interpretation, since the final state (ethylidyne plus $\frac{1}{2}$ H_{2(g)}) is reached quickly at 300 K and 0.17 ML.

5.1.1. QVB method

The definition of the diabatic bond dissociation energy yields $D(\text{Pt}_n\text{--CCH}_3)$ to be given by



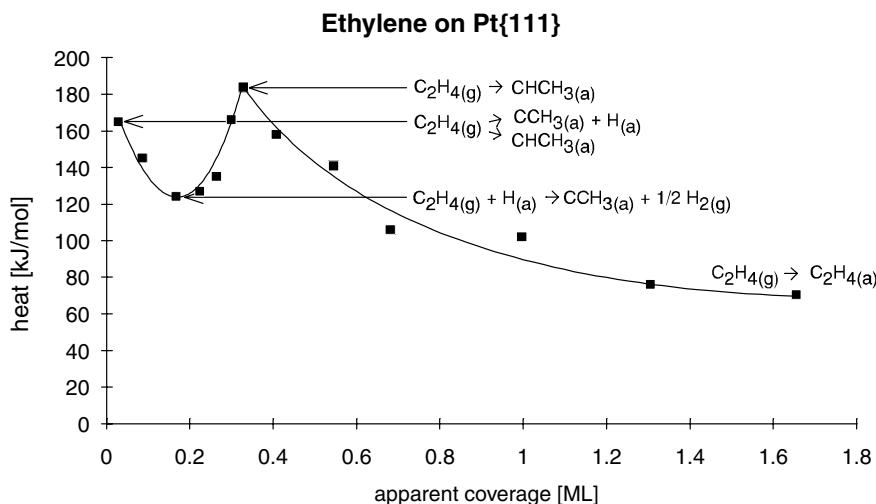


Fig. 3. Experimental data measured by microcalorimetry of ethylene adsorption and decomposition on Pt{111} at 300 K as published by Yeo et al. [17] with the final assignments supported by spectroscopic and thermochemical data. The solid line through the data points is only to guide the eye.

and so

$$\begin{aligned}
 & -D(\text{Pt}_n\text{-CCH}_3) \\
 &= \Delta H_f^\ominus(\text{CCH}_3(\text{a})) - \Delta H_f^\ominus(^4\text{E} \cdot \text{CCH}_3(\text{g})) \\
 &= -71.7 \text{ kJ/mol} - \Delta H_f^\ominus(^4\text{E} \cdot \text{CCH}_3(\text{g})) \quad (11)
 \end{aligned}$$

Thus, we only need $\Delta H_f^\ominus(^4\text{E} \cdot \text{CCH}_3(\text{g}))$ to determine $D(\text{Pt}_n\text{-CCH}_3)$. This is the difficult part since no experimental or theoretical determination of this quantity is available. Until this situation is resolved, most likely by ab initio theory in the near future, Carter and Koel's [26] work provides a good estimate for this value as $639 \pm 14.6 \text{ kJ/mol}$ from the heat of formation of the ground state of the radical $\Delta H_f^\ominus(^2\text{ECH}_3\text{C}\cdot) = 569 \pm 14.6 \text{ kJ/mol}$ and an approximate value for the $^4\text{E}-^2\text{E}$ splitting in CH_3C by using the $^4\Sigma-^2\Pi$ splitting in HC (69.9 kJ/mol). Using this value of $\Delta H_f^\ominus(^4\text{E} \cdot \text{CCH}_3(\text{g})) = 639 \text{ kJ/mol}$ leads to a value for $D(\text{Pt}_n\text{-CCH}_3)$ of 711 kJ/mol . If one now attempts to assign an average Pt-C σ bond dissociation energy, then $D(\text{Pt-C}) = \frac{1}{3}D(\text{Pt}_n\text{-CCH}_3)$ and we determine a value of $D(\text{Pt-C}) = 237 \text{ kJ/mol}$.

5.1.2. The ABE method

Again looking at reaction (1), we can now use the ABE method in its first-order approximation

to determine $D(\text{Pt-C})$. This has already been reported by Yeo et al. [17], but is explained in greater detail here.

The measured heat of reaction ($\Delta H_{r \times n}$) is -124 kJ/mol . To avoid breaking multiple bonds in a single step, the process can be described as follows: We start with ethylene plus Pt_n . A C-H bond is cleaved in the first step, to make $\text{CH}=\text{CH}_2$ plus H ($D(\text{C-H}) = 465 \text{ kJ/mol}$, the adiabatic bond dissociation enthalpy in $\text{H}_2\text{C}=\text{CH}_2$ [31]). The H atom is converted to $\frac{1}{2}\text{H}_2$ gas, which is downhill by one-half of the H-H bond energy ($-436/2 = -218 \text{ kJ/mol}$) [31]. Then, the $\text{CH}=\text{CH}_2$ is bonded to the Pt surface at the CH carbon ($-D(\text{C-Pt})$). The C=C bond is broken ($D(\text{C=C}) = 733 \text{ kJ/mol}$ in $\text{H}_2\text{C}=\text{CH}_2$) [31] and replaced with a C-C single bond ($D(\text{C-C}) = 376 \text{ kJ/mol}$ in $\text{CH}_3\text{-CH}_3$) [31] and a C-Pt σ bond at the same C atom ($-D(\text{C-Pt})$). Next, a C-H bond on the CH carbon atom is shifted to the other (CH_2) carbon atom, and replaced with a C-Pt σ bond to make $\text{CH}_3\text{C}(\text{a})$ ($-D(\text{C-Pt})$).

The net reaction is then ethylene plus Pt_n going to adsorbed ethylidyne plus $\frac{1}{2}\text{H}_2$ gas, and its net energy is:

$$\begin{aligned}
 \Delta H_{r \times n} &= D(\text{C-H}) - \frac{1}{2}D(\text{H-H}) + D(\text{C=C}) \\
 &\quad - D(\text{C-C}) - 3D(\text{C-Pt}) \quad (12)
 \end{aligned}$$

Finally the average Pt–C σ bond energy is calculated by rearranging this equation to get $D(\text{Pt–C})$ on one side:

$$\begin{aligned} D(\text{Pt–C}) &= \frac{1}{3}D(\text{Pt}_n\text{–CCH}_3) \\ &= \frac{1}{3}[-\Delta H_{r \times n} + (D(\text{C=C}) \\ &\quad - D(\text{C–C}) + D(\text{C–H}) \\ &\quad - \frac{1}{2}D(\text{H–H}))] \\ &= \frac{1}{3}[-\Delta H_{r \times n} + (733 - 376 + 465 \\ &\quad - 218) \text{kJ/mol}] \\ &= \frac{1}{3}(728 \text{kJ/mol}) = 243 \text{kJ/mol} \quad (13) \end{aligned}$$

Note that this calculation involves the use of the most appropriate average bond energies for that specific molecule and bond. If instead we used tabulated ABE values from tables such as Tables 1 and 2 which average over a large series of related molecules, a slightly different result would be obtained. For example, the ABE for C–H bonds at normal primary carbons is 410 kJ mol from Table 1, and would give 225 kJ/mol for $D(\text{Pt–C})$ if used for $D(\text{C–H})$ in the above equation. Using only the most appropriate average C–H and C–C BDEs from Table 1, and the C=C BDE of for ethylene of 733 kJ/mol [31], the ABE method gives $D(\text{C–Pt}) = 246 \text{kJ/mol}$ instead. Either value of $D(\text{C–Pt})$ estimated by this ABE method (243 or 246 kJ/mol) agrees fairly well with the value determined from the QVB method above, 237 kJ/mol. They also agree closely with C–Pt σ bond energies determined on other Pt faces by the ABE method [11].

5.2. Interpretation of the coverage dependence of the heat in terms of M–C bond energies

As shown in Fig. 3 and Table 3, three different reactions have been assigned [17] to different stages in the interaction of ethylene with Pt{111}, corresponding to the measured reaction energy at zero coverage (-174kJ/mol), a minimum (-124kJ/mol) at $\theta \approx 0.2 \text{ML}$, and a maximum (-184kJ/mol) at $\theta \approx 0.3 \text{ML}$ in the measured SCAC curve. These assignments are supported by previous spectroscopic investigations [32,33] and thermodynamic considerations [26]. We have calculated average Pt–C σ bond energies with both ap-

Table 3

Reactions assigned by Yeo et al. [17] to the measured reaction heats in the adsorption and decomposition process of ethylene on Pt{111}

		$\Delta_r H$ (kJ/mol)
I	$\text{C}_2\text{H}_{4(\text{g})} \rightarrow \text{CCH}_{3(\text{a})} + \text{H}_{(\text{a})}$	-174
I'	$\text{C}_2\text{H}_{4(\text{g})} \rightarrow \text{CHCH}_{3(\text{a})}$	-174
II	$\text{C}_2\text{H}_{4(\text{g})} + \text{H}_{(\text{a})} \rightarrow \text{CCH}_{3(\text{a})} + \text{H}_2$	-124
III	$\text{C}_2\text{H}_{4(\text{g})} \rightarrow \text{CHCH}_{3(\text{a})}$	-184

Table 4

$\langle D(\text{Pt–C}) \rangle$ calculated with either the QVB method or the ABE method

	QVB-method $\langle D(\text{Pt–C}) \rangle$ in kJ/mol	ABE-method $\langle D(\text{Pt–C}) \rangle$ in kJ/mol
I	263	228
I'	240.7	265.5
II	237	225
III	245.8	270.5
Average	246.6	247.3

proaches (see Table 4) for each of the reactions. At zero coverage we take both the formation of ethynyl plus adsorbed hydrogen (reaction I) and that of ethylidene (reaction I') into account. The SCAC system does not provide a means of distinguishing between these reactions, which would require a spectroscopic technique, but it is reasonable to assume that steady state is reached in these competing pathways, yielding thermochemical results and a derived value for $D(\text{Pt–C})$ for each process. The overall average Pt–C bond energy obtained by the QVB and ABE methods are 246.6 and 247.3 kJ/mol, respectively, averaged over all four reactions.

A large amount of variability in Table 4 is introduced by the uncertainty of the assignments of specific reactions to the observed heats and also by real finite coverage (coadsorption) effects on the heats. If one of the reaction assignments is incorrect, the value of $D(\text{Pt–C})$ for this process will not agree with the others. For example, the use of two different heats for the same reaction expressed in reactions I' and III cause scatter in the results. In addition, we should expect different values because of the two different methods used to calculate $D(\text{Pt–C})$ for each process.

A closer look at the individual reactions should prove of interest. As can be seen from Table 3, depending on coverage there are two different products for the ethylene decomposition process on Pt{111}: ethylidene (CHCH_3), with two σ bonds to the surface, and ethylidyne (CCH_3), with three σ bonds. The ABE results in Table 4 suggest that the M–C bond strength weakens as the number of M–C bonds increases. There is a difference of about 42 kJ/mol in the Pt–C bond strength as the number of Pt–C σ bonds formed changes from two (reaction I' and III) to three (reactions I and II). This is similar to the trends in Tables 1 and 2, where the bond energy to a carbon atom weakens as more of its H neighbors are replaced with R groups (alkyls), starting from H-CH_3 . This suggests that substituent effects due to Pt neighbors are more like those of R groups than H. This trend is not supported by the results of the QVB approach, however, which indicates that little importance should be attached to this trend. We conclude that this set of experimental data [17] provides a single consistent but average value for the Pt–C bond dissociation energy.

6. Discussion and conclusions

Several theoretical studies of hydrocarbon–Pt bond energies have been made, based on atom superposition and electron delocalisation molecular orbital theory [34], the extended Hückel method [35] and, most recently, density functional theory [23,36]. The latter is regarded as the most accurate [12], and yielded geometric structure, the adsorption energy, and the Pt–C bond energy (244 kJ mol^{-1}) [23] in excellent agreement both with the LEED structure for ethylidyne on Pt{111} [37] and with the SCAC experimental heats [17]. An early, but high level, calculation of Pt– CH_3 by Carter and Goddard [38,39] gave $D(\text{Pt-C}) = 222 \text{ kJ/mol}$. Our analysis of experimental calorimetric data for the ethylene reaction with Pt{111} by two independent approaches produce very similar values for an estimate of the average Pt–C σ bond energy in ethylidyne adsorbed on Pt, viz. 237 kJ/mol (QVB method) and 243 kJ/mol (ABE method). These are average values obtained

for a carbyne carbon atom multiply bonded to the surface, and are in close agreement with the DFT result for the same system [23]. It clearly would also be useful for microcalorimetry to be done for adsorbed methyl, where the Pt–C single bond energy is directly probed.

The agreement between the two approaches discussed is quite good. One could ask why did the calculations using the ABE approach work out so well? This is because the “spin-impurity” problem discussed earlier is simply avoided. Thus, in this case the ABE approach is extremely simple and yields a very useful first estimate of surface bond energies. Using this method, values have also been derived from SCAC experiments for $D(\text{Rh-C}) = 268 \text{ kJ mol}^{-1}$ [4] and $D(\text{Ni-C}) = 204 \text{ kJ/mol}$ [6].

Clear assignments of surface species formed during adsorption at given coverages in the microcalorimetry experiment are required for the determination of any metal–carbon bond strength, which may be based either on spectroscopic observations or on the thermodynamic analysis itself.

In the analysis of this data, one must carefully consider the nature of the surface chemical bond: covalent, ionic, and/or dative. Thus far, we have considered only contributions from covalent bonding. Even for purely covalent bonding, it is important to distinguish between σ and π bonds, since these have different character and strength in organometallic complexes. For ethylidyne, it is clear from the bond lengths in the adsorbed species determined from LEED crystallography [37] and in the ligand in the tricobalt cluster compound determined using X-ray crystallography [40], along with the C–H stretching frequency in the vibrational spectroscopy of both species [40], that there is little or no hyperconjugation in adsorbed ethylidyne on Pt{111} and it may safely be regarded as bound to the surface through an sp^3 -hybridized carbyne carbon via three Pt–C covalent σ bonds. This is in fact the clear conclusion from the DFT study [23]. This should be the case for ethylidyne adsorbed on other metal surfaces, where the attachment of the carbyne carbon to a methyl group implies sp^3 hybridisation, but not necessarily true in general for adsorbed hydrocarbon species. An accounting will need to be made for the relative contribution of σ and π bonds to the sur-

face, and a determination or estimation of the π bond strength is required, as carried out for various hydrocarbons on Pt{111} [26]. Care must be taken, particularly without spectroscopic evidence, in the use of ethylene or acetylene molecular chemisorption energies to determine metal–carbon bond strengths. The hybridisation of these two molecules on the surface may range from sp^2 to sp^3 for ethylene, and sp to sp^3 for acetylene. The relative contributions of σ and π bonding to the surface may therefore be indeterminate in some cases. However, prior knowledge of the M–C σ bond strength, for example from the study of ethynylidyne adsorption, clearly provides a means of estimating the π contribution in these cases.

Care also must be taken in discussing the type of Pt–C σ bond one is considering. Recent calorimetric measurements of benzene molecular adsorption on Pt(111) in a structure parallel to the surface provides the average energy of a different type of Pt–C bond than that described above, namely that associated with the σ donation of electrons from the carbons' sp^2 orbitals into antibonding Pt orbitals (with some π -backbonding as well), where these sp^2 orbitals are still dominated by their intramolecular C–C π bonding in benzene's aromatic ring. These Pt–C bonds were found to have an average energy of ~ 33 kJ/mol [41].

A limitation in the QVB method is the neglect of ΔH_r for the weakening of the Pt–Pt bonds due to adsorption. This is a negligible factor for Pt{111}, being in the region of 5 kJ/mol [23], but in general this value is unknown and could be larger for other metals. This factor is quite significant for adsorption that occurs accompanied by a significant reconstruction of the surface [4]. However, it has been demonstrated that this contribution can be measured experimentally [1,4], and estimated theoretically by DFT [23,42].

There are many directions for this work to take. Obviously, an important goal is to determine adsorbate bond energies on a wide variety of metal surfaces [23,4,6]. Tabulating M–C σ bond energies for many of the late transition metals would be a tremendously valuable endeavor. A key issue to be evaluated is whether $D(M-C)$ strongly depends on the local electronic and geometric structure of the metal surface, and, as would be expected, on

the coordination of metal atoms at the surface [1,7,43]. For example, will $D(M-C)$ strongly depend on the metal crystal face? This evaluation will be a difficult one in general, since it depends on the same species forming on different crystal faces when it is well known that different faces often lead to different reaction pathways. A first comparison of $D(Pt-C)$ on different Pt surfaces after the adsorption of either acetylene or ethylene leads to the conclusion that this quantity is relatively insensitive to the surface plane⁵. In addition, comparing adsorption heats for different gases that produce small adsorbed hydrocarbon fragments bound by one, two and three M–C bonds could reveal the dependence of $D(M-C)$ on the number of M–C bonds to a given C atom. Our preliminary results with the ABE method suggest that the additional bonds to the metal have substituent effects similar to an additional alkyl group: the M–C bond will weaken as more M ligands replace H ligands. It is important to examine the possible contribution of π bonding in the more dehydrogenated species. The uncertainty in determining the heat of formation of the gas phase radical required by the QVB approach increases strongly with increasing dehydrogenation and this limits the determination of small differences in metal–carbon bond energies. The “spin impurity” problem also becomes more severe in the ABE approach in these situations. Another key point to be evaluated is whether the metal–carbon bond energy depends on the nature of the hydrocarbon molecule or fragment adsorbed. Siegbahn [44] has shown in his calculations that $D(Pd-R)$ is the same for $R = CH_3, C_2H_5$ and C_3H_7 , and suggested that this was a general result for the late transition metals. This prediction can be checked, in principle, using SCAC.

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