

## LINKING CHEMICAL PHYSICS AND SURFACE SCIENCE: THERMOCHEMISTRY OF ADSORBATES FROM PURELY GAS PHASE DATA

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A scheme is presented for calculating the heats of formation of adsorbed species on metal surfaces using only two pieces of gas phase data, both of which are available from either theory or experiment. Using this quasiempirical valence bond (QVB) approach, heats of adsorption and adsorbate-surface bond strengths can be estimated, yielding predictions of surface thermochemistry and reaction mechanisms. The power of this method lies in its ability to predict heats of adsorption and formation of molecular fragments that do not readily desorb on their own (e.g. reactive radicals), and thus do not lend themselves to direct measurements of their heats of adsorption.

### 1. Introduction

Experimental studies of the interactions of gases with metal surfaces have afforded much structural information about adsorbed atoms and molecules, but equivalent progress in understanding surface reaction mechanisms has been limited. In particular, most thermochemical data for adsorbates (e.g. the relative stabilities of various surface species) are completely unknown. Identification of viable intermediates is crucial for determining reaction pathways and at present is rarely achievable experimentally. Temperature-programmed desorption (TPD) is the primary experimental technique available for measuring heats of adsorption. However, this method requires additional information if adsorption is activated and generally detects only the desorption of species that are stable in the gas phase, i.e. mostly closed shell molecular adsorbates. Unfortunately, TPD is useless for determining heats of adsorption for many adsorbates, e.g. hydrocarbon fragments, since the barriers to subsequent surface reactions are less than the corresponding desorption activation energies. The barriers to desorption can be unusually high because of both large adsorbate-surface bond energies and because the final products in the gas phase may be highly energetic, unstable radical fragments.

As an example, consider the individual steps in the Haber process for catalytically synthesizing ammonia from  $N_2$  and  $H_2$ . While surface scientists have been able to measure the heats of adsorption of  $N_2$  (molecular and dissociative adsorption),  $NH_3$  (molecular adsorption) and  $H_2$  (dissociative adsorption) on a variety of metal surfaces [1-3], the thermochemistry of the other intermediate steps is unknown because the heats of adsorption of  $NH$  and  $NH_2$  are unmeasurable at present. This inhibits our ability to assess the thermodynamics of  $N_{(a)} + H_{(a)} \rightarrow NH_{(a)}$ ,  $NH_{(a)} + H_{(a)} \rightarrow NH_{2(a)}$ , and  $NH_{2(a)} + H_{(a)} \rightarrow NH_{3(a)}$ . While ultimately kinetic barriers will dictate preferred reaction pathways, the thermodynamic propensity for a reaction to occur is still an important quantity to determine.

This example illustrates the great need for accurate estimates of heats of adsorption for unstable surface intermediates. With such estimates in hand, it will be possible to predict heats of reaction for a wide variety of elementary processes occurring on surfaces. It is essential to find a way to estimate this equilibrium thermodynamic data for adsorbed atoms and molecular fragments that do not readily desorb from surfaces. This paper presents a novel quasiempirical valence bond (QVB) scheme for obtaining such estimates. The approach has been applied successfully toward understanding the mech-

anism of ethylene decomposition on Pt(111) [4], but should be general for any reaction on any metal surface. The success of the method is inhibited only by the existing limited supply of gas phase data. The future looks bright, however, since theoretical and experimental chemical physicists can provide the much needed values that will make this technique tremendously useful. The power of this technique lies in its simplicity (i.e. both experimentalists and theoreticians will be able to employ it with equal ease without resorting to extensive computational facilities) and in its predictive capability to fill in the gaps between experimentally measurable quantities and those currently impossible to measure.

## 2. Theoretical method

The essence of the QVB method is to ascertain the *appropriate local electronic state of the adsorbate when bonded to the metal surface*, as in the valence bond approach to molecular electronic structure. Once this is understood, the rest of the calculation follows simply and naturally, as outlined below.

In order to calculate the desired heats of formation of adsorbates on metal surfaces, we will construct a thermodynamic cycle beginning with the electronic ground state of the gas phase species and ending with the adsorbed atom or molecule. Direct construction of this cycle requires that the heats of formation of the corresponding gas phase species and the surface-adsorbate bond energies both be known. In general, these adsorbates correspond to gas phase molecular fragments that are relatively unstable (i.e. radicals or excited states) and hence their heats of formation have not been measured. Furthermore, most surface-adsorbate bond energies for such fragments are also unavailable. We now describe how to circumvent these problems.

Construction of this cycle will require knowledge of the metal-adsorbate bond character and two pieces of data that can be supplied by gas phase experiments or theory. The procedure is as follows: (i) determine how many chemical bonds are formed from the adsorbate to the surface and characterize them according to either primarily covalent, ionic, or donor-acceptor character; (ii) obtain the experimental heat of formation for the gaseous species in its ground

electronic state (or estimate it via a Born-Haber cycle of known heats of formation and bond dissociation energies); (iii) use electronic excitation energies, electron affinities, or ionization potentials to calculate a heat of formation for *a gas phase species that most resembles the local electronic state of the molecule when it is adsorbed on the surface*; and finally (iv) use measured heats of adsorption (where available) or use estimated or calculated bond energies (from, for example, ab initio electronic structure calculations) for  $\sigma$  and  $\pi$  covalent, ionic, or donor-acceptor bonds [5] to predict the heat of formation of the adsorbed species by subtracting the adsorbate-surface bond energies from the gas phase heats of formation.

The first step of this approach is to determine the nature of the bond between the metal and the adsorbate. This can be extracted from surface vibrational spectroscopy (high resolution electron energy loss (HREELS) or infrared (IR) spectroscopy), from geometries obtained via low energy electron diffraction (LEED) intensity analyses or via near edge X-ray absorption fine structure (NEXAFS) data, from ultraviolet or X-ray photoemission (UPS or XPS) data that reveal electronic structural information, from X-ray diffraction on analogous organometallic cluster complexes, from ab initio theoretical calculations, or simply from chemical intuition.

Essentially, one needs to decide whether the adsorbate-metal bonding is of ionic, covalent, or of donor/acceptor character (or perhaps a mixture of the three) and then to determine the appropriate metal-adsorbate bond order. This is the key step in setting up cycles to calculate heats of adsorption: *the metal-adsorbate bond character so determined will indicate the electronic state of the free adsorbate appropriate for forming the surface-adsorbate bond*. If the bonding is primarily donor/acceptor-like, e.g. in CO, this method is unnecessary since TPD will yield reliable heats of adsorption for such species. Hence we concentrate on those species that have either covalent or partially ionic character in their interaction with the metal surface. (Electronegative adsorbates may have largely ionic bonds to the surface, however, the adsorption-induced charge transfer will reverse itself upon desorption, in order to desorb a neutral spe-

cies. Thus, the current analysis should hold for ionic bonds as well.)

A simple example is provided by one of the postulated intermediates in the Haber process (vide supra),  $\text{NH}_{(a)}$ . Little is known about the structure of  $\text{NH}_{(a)}$  experimentally, but simple chemical intuition indicates that NH is likely to form two partially covalent/partially ionic sigma bonds to the metal surface in a bridging configuration (based on the fact that nitrogen is trivalent and reasonably electronegative). Two bonds from NH to the metal require two initially unpaired electrons on NH (i.e. a triplet). Thus the appropriate electronic state for bonding NH to a metal surface is the  $^3\Sigma^-$  state, which happens to be the ground state of NH.

Another example which illustrates the need for further data from the chemical physics community is the adsorption of CH on metal surfaces, proposed as an intermediate in many heterogeneously catalyzed processes, from Fisher-Tropsch production of hydrocarbons and oxygenates to hydrocarbon cracking and reforming. Since a carbon atom is tetravalent and less electronegative than a nitrogen atom, we expect CH to prefer to form three primarily covalent sigma bonds to the metal surface, in a bridging configuration. This bonding picture is indirectly confirmed by LEED analysis [6] of the structure of the related species,  $\text{CCH}_{3(a)}$ , which indeed is triply bridging with three equivalent sigma bonds between carbon and the metal surface. Three metal-carbon bonds require three initially unpaired electrons on carbon; thus we conclude that the appropriate electronic state for bonding CH to a metal surface is the  $^4\Sigma^-$  state. This is the first excited electronic state of CH, with the ground state being  $^2\Pi$ . Thus, since gaseous CH exists primarily in the nonbonding  $^2\Pi$  ground state, we must know the gas phase electronic excitation energy required to put the adsorbate precursor in the electronic state appropriate for bonding. While this is a well known quantity for CH ( $\Delta E(^4\Sigma^- - ^2\Pi) = 16.7$  kcal/mol; ref. [7]), very few of these electronic excitation energies have been measured or calculated theoretically for other important species such as the infamous  $\text{CCH}_3$  (an extremely well characterized adsorbate [1]). The need for these values in the cycle presented below hopefully will provide greater impetus for future spectroscopic and ab initio theoretical studies.

Thus, the second step in setting up the cycle for estimating heats of adsorption involves obtaining two pieces of data: (i) the gas phase electronic excitation energy discussed above and (ii) a characteristic metal-ligand (M-X) single bond energy from theory or experiment. The M-X single bond energy should preferably be taken from data for a coordinatively saturated metal complex, so that spin-coupling effects [8] do not perturb the bond energy (since spin-coupling effects are not expected to be important on a metal surface). Hence we need characteristic metal-carbon, metal-nitrogen, metal-hydrogen, and metal-oxygen single bond strengths from  $D(\text{M}^{\text{sat}}-\text{CH}_3)$ ,  $D(\text{M}^{\text{sat}}-\text{NH}_2)$ ,  $D(\text{M}^{\text{sat}}-\text{H})$ , and  $D(\text{M}^{\text{sat}}-\text{OH})$ , where  $\text{M}^{\text{sat}}$  represents a coordinatively saturated metal center. Unfortunately, most of the M-X bond strengths that have been measured or calculated are for coordinatively unsaturated metal complexes, where electronic exchange energies can dramatically affect the bond dissociation energy. However, we have recently reported a means of converting such values into quantities appropriate for coordinatively saturated metal complexes, thereby negating anomalous spin-coupling effects [8]. This method, used in conjunction with theoretical predictions of bond energies or measured values from ion beam [9], kinetic energy release distribution [9], ion cyclotron resonance [10], or photoacoustic calorimetric [11,12] studies, will provide the needed values if they are unavailable directly.

Once the electronic excitation energy and characteristic bond energy are in hand, the cycle is set up, as shown for CH in fig. 1. Essentially we start from the ground electronic state of the gaseous species to be adsorbed, excite the molecule into the electronic state appropriate for adsorption (this may (e.g. CH) or may not (e.g. NH) be necessary, depending on whether the ground state is already appropriate for adsorption), and then adsorb the molecule onto the surface. The relevant quantities necessary for estimating the heat of adsorption are: (i) the heat of formation for the gaseous species in its ground electronic state; (ii) the electronic excitation energy and perhaps the electron affinity or ionization potential; (iii) the metal-adsorbate bond order  $N$ ; and (iv) characteristic single bond energies for  $\sigma$  and  $\pi$  covalent or donor-acceptor metal-ligand bonds. Starting with the heat of formation of X ( $\Delta H_f(X_{(g)})$ ), we

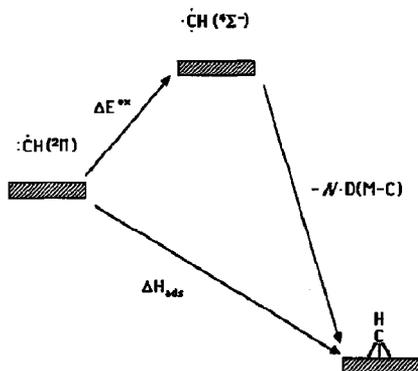


Fig. 1. Thermodynamic cycle for adsorption of gaseous CH on a metal surface. Excitation of the  ${}^2\Pi$  ground state of  $\text{CH}_{(g)}$  to the  ${}^4\Sigma^-$  excited state (with a cost of  $\Delta E^{\text{ex}}$ ) is necessary in order for three bonds to be formed from the carbon atom to the surface.  ${}^4\Sigma^- \text{CH}_{(g)}$  is then adsorbed on the surface, lowering the energy of the system by the adsorbate-surface bond energy,  $ND(M-C)$ , where here the bond order  $N=3$  and  $D(M-C)$  is a characteristic metal-carbon single bond energy. The heat of adsorption,  $\Delta H_{\text{ads}}$ , is simply  $\Delta E^{\text{ex}} - ND(M-X)$ .

add the excitation energies necessary to put the molecule into the appropriate bonding state ( $\Delta E^{\text{ex}}$ ), and then we subtract  $N$  times the characteristic bond energy  $D(M-X)$  (as an estimate for the actual adsorbate-surface bond energy) to arrive at the heat of formation of  $X_{(a)}$ ,

$$\Delta H_f(X_{(a)}) = \Delta H_f(X_{(g)}) + \Delta E^{\text{ex}} - ND(M-X).$$

The heat of adsorption is simply

$$\Delta H_{\text{ads}} = \Delta H_f(X_{(a)}) - \Delta H_f(X_{(g)}).$$

To illustrate how the scheme works, we will consider a simple example of the adsorption of CH on Pt(111). As discussed above, CH should have three equivalent sigma bonds between carbon and the metal surface, requiring the  ${}^4\Sigma^-$  state as the bonding state of CH, up 16.7 kcal/mol from the  ${}^2\Pi$  ground state. A Pt-CH<sub>3</sub> bond energy of 53 kcal/mol has been calculated for a coordinatively saturated complex by Low and Goddard [13]. Several Pt-CH<sub>3</sub> bond energies in coordinatively saturated complexes have been measured:  $D_e(\text{cis}-(\text{PEt}_3)_2(\text{CH}_3)\text{Pt}-\text{CH}_3) = 52 \pm 3$  kcal/mol,  $D_e(\text{cis}-(\text{PEt}_3)_2(\text{Cl})\text{Pt}-\text{CH}_3) = 47 \pm 7$  kcal/mol, and  $D_e(\text{cis}-(\text{PPh}_3)_2(\text{I})\text{Pt}-\text{CH}_3) = 45 \pm 9$  kcal/mol [14]. These values yield  $51 \pm 3$  kcal/mol (weighted average) for the Pt-CH<sub>3</sub> bond strength.

The theoretical bond energy is in excellent agreement with experiment, indicating no large errors are associated with the ab initio calculations (typically  $\approx 2$  kcal/mol) and hence we use  $53 \pm 2$  kcal/mol for  $D_e(\text{Pt}-\text{CH}_3)$ . Starting with the heat of formation of  ${}^2\Pi$  CH of 136.0 kcal/mol [15], we add 16.7 kcal/mol to obtain the heat of formation of  ${}^4\Sigma^- \text{CH}$  and then subtract  $3 \times 53 = 159 \pm 3$  kcal/mol, to obtain a heat of formation of  $\text{CH}_{(a)}$  of  $-6 \pm 3$  kcal/mol and a heat of adsorption of  $-142 \pm 3$  kcal/mol. The negative of the heat of adsorption yields the surface-adsorbate bond energy,  $D(\text{Pt}_{(s)}-\text{CH}) = 142 \pm 3$  kcal/mol. Currently, there are no experimental measurements with which to compare these estimates for CH on Pt(111) and thus our approach is the only means of estimating the thermochemistry of  $\text{CH}_{(a)}$  without resorting to detailed calculations.

One adsorption energy that is well known from experiment is that for ethylene on Pt(111) and hence we use its heat of adsorption to assess the accuracy of our approach. The vertical singlet-triplet ( ${}^1A_1 \rightarrow {}^3B_{3u}$ ) excitation energy in gaseous ethylene is  $\Delta E_{\text{ST}} \approx 99$  kcal/mol [16], while ab initio CI calculations predict 101 kcal/mol [17]. If we subtract two Pt-C  $\sigma$  bond energies ( $106 \pm 3$  kcal/mol) from  $\Delta E_{\text{ST}}$ , we obtain a value of  $7 \pm 3$  kcal/mol for the heat of adsorption of ethylene. However, in contrast to CH adsorption, the geometry of adsorbed ethylene is significantly different from that of the (vertically) electronically excited state in the gas phase (which is, of course, just the ground state geometry). Indeed, the vertical excitation energy merely provides an upper bound on the appropriate excitation energy for ethylene and therefore a lower bound on the binding energy of ethylene to the surface. The adiabatic singlet-triplet excitation energy for gaseous ethylene is  $70 \pm 2$  kcal/mol [17], where the equilibrium structure of the triplet has a much longer C-C bond (1.56 Å) and is nonplanar, with the CH<sub>2</sub> groups twisted by 90° with respect to each other. NEXAFS studies [18] indicate that adsorbed ethylene on Pt(111) has an elongated C-C bond ( $R_{\text{C-C}} = 1.49 \pm 0.03$  Å), while HREELS data do not suggest that the CH<sub>2</sub> groups are twisted with respect to one another [19]. Ab initio calculations on the singlet-triplet splitting in C<sub>2</sub>H<sub>4</sub> as a function of the geometry [17] predict a singlet-triplet splitting of  $85 \pm 2$  kcal/mol when planar ethylene is allowed a 1.49 Å C-C bond in the

triplet state. The error bars on the experimental C–C bond length ( $\pm 0.03 \text{ \AA}$ ) correspond to errors of  $\pm 2 \text{ kcal/mol}$  in the singlet–triplet splitting, which is also the inherent error in the *ab initio* value [17]. By using  $85 \pm 2 \text{ kcal/mol}$  for the appropriate electronic excitation energy and then subtracting  $106 \pm 3 \text{ kcal/mol}$  for the two sigma bonds, we obtain a predicted heat of adsorption of  $21 \pm 4 \text{ kcal/mol}$ , while the experimental value is  $17 \pm 2 \text{ kcal/mol}$  from TPD [20]. The predicted value is slightly high, however, the experiment is carried out under high coverage conditions where repulsive interactions may lower the ethylene–platinum bond strength. Thus, our calculations (that do not consider repulsive interactions) are expected to be in excellent agreement with an experimental determination of the ethylene–platinum bond energy at lower coverages.

As experimental geometries of adsorbates become more widely available, the method outlined above will be increasingly useful for determining surface–adsorbate interactions in a quantitative manner. Ethylene is only one example. We have used what information is available in the literature to treat a variety of other hydrocarbon fragments on platinum surfaces; this work is reported elsewhere [4].

### 3. Concluding remarks

In summary, we have presented a QVB scheme for calculating heats of formation of adsorbates on metal surfaces. With heats of formation of adsorbates in hand, heats of reaction can be calculated for any metal surface processes that involve these species. The predictions will be reliable to the extent that the bonding of the adsorbate to the metal is well understood and the necessary excitation energies and characteristic bond energies are well determined.

This simple analysis is not intended for applications to semiconductor surfaces, where strong covalent bonding between surface atoms prevails, since adsorption of gases on these surfaces strongly perturbs the nature of the crystal in the near surface layers. It is also not appropriate for metal oxide surfaces, where the presence of the oxide may strongly perturb the adsorbate–metal bond. In particular, this approach is expected to be most successful for clean

metal surfaces which do not undergo substantial reconstruction upon adsorption of gases.

The lack of an adequate gas phase thermochemical and spectroscopic data base still prevents this technique from general utility. However, it should provide new motivation for chemical physicists to measure electronic excitation energies in simple organic fragments and bond dissociation energies in coordinatively saturated organometallic complexes. Furthermore, it compels surface scientists to utilize the available gas phase data base in conjunction with the ideas presented here to help analyze their mechanistic observations. As the gas phase data base grows in number and accuracy, this method will become more and more powerful for assessing surface reaction mechanisms.

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