

Bond Energies of Molecular Fragments to Metal Surfaces Track Their Bond Energies to H Atoms

Eric M. Karp,^{‡,†} Trent L. Silbaugh,[‡] and Charles T. Campbell^{*,‡,§}

[‡]Department of Chemical Engineering and [§]Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700, United States

ABSTRACT: The bond energy of molecular fragments to metal surfaces is of great fundamental importance, especially for understanding catalytic reactivity. Thus, the energies of adsorbed intermediates are routinely calculated to understand and even predict the activity of catalytic materials. By correlating our recent calorimetry measurements of the adiabatic bond dissociation enthalpies of three oxygen-bound molecular fragments [-OH, -OCH₃, and -O(O)CH] to the Pt(111) surface, it is found that these RO–Pt(111) bond enthalpies vary linearly with the RO–H bond enthalpies in the corresponding gas-phase molecules (water, methanol, and formic acid), with a slope of 1.00. This parallels the known trend for organometallic complexes, thus highlighting the local character of chemical bonding, even on extended metal surfaces. This allows prediction of bond enthalpies for many other molecular fragments to metal surfaces, and the energetics of important catalytic reactions.

Understanding the energetics of chemical reactions on transition metal surfaces is important to many technologies, including efforts to develop better catalysts for the production of clean fuels, the combustion of fuels, and the production of chemicals with improved energy efficiency and less pollution, and in developing better fuel cells and batteries. Thus, one would like to be able to estimate the bond energies of adsorbed molecular fragments to transition metal surfaces. We show here a simple trend with powerful predictive ability in that respect.

With organometallic complexes in liquid solutions, equilibrium measurements have yielded the σ bond energies of many ligands to metal centers, and these bond strengths have been shown to correlate strongly with the corresponding gas-phase ligand-to-hydrogen bond strength.^{1–3} Specifically, Bryndza and co-workers showed that when the gas-phase hydrogen-to-ligand bond strength is plotted versus the ligand bond strength to a given metal center, the data fall approximately on a straight line with a slope equal to 1.00. This relationship allows the bond strengths of many other ligands to metal centers to be estimated simply from the corresponding hydrogen-to-ligand bond strengths in gas-phase molecules, which are very well known.^{4,5} It has been suggested that this trend should also hold for adsorbates bound to metal surfaces⁶ based on an earlier qualitative observation.⁷ A similar linear relationship between metal–C bond energies for adsorbed alkyls and H–C bond energies in the corresponding gaseous alkanes was predicted on the basis of density functional theory (DFT) to hold on several

late transition metal surfaces, albeit with a different slope.^{8,9} We show here, for the first time, that such a relationship does indeed hold with unit slope for experimental bond energies of ligands bound to a late transition metal surface, Pt(111). We further discuss this discovery's predictive ability for estimating the bond energies of molecular fragments adsorbed to transition metal surfaces and demonstrate how this relationship can be used to gain considerable insight into the thermodynamics of important catalytic reaction mechanisms.

Table 1 lists the adiabatic Pt–OR bond dissociation enthalpies for three oxygen-bound molecular fragments to the Pt(111) surface: deuterated hydroxyl (OD),¹⁰ monodentate formate (O(O)CH),¹¹ and methoxy (OCH₃),¹² recently measured by single-crystal adsorption calorimetry. Also listed are these adsorbates' corresponding gas-phase hydrogen-to-ligand bond enthalpies: H–OD for deuterated hydroxyl, H–O(O)CH for monodentate formate, and H–OCH₃ for methoxy. In Figure 1, the measured bond enthalpies for these adsorbates to Pt(111) are plotted versus their corresponding hydrogen-to-ligand adiabatic bond dissociation enthalpies. Similar to the work of Bryndza et al.¹ for organometallic complexes, we find that a straight line with a slope of 1.00 ($y = x - 249$ kJ/mol) fits these data very well, with a standard deviation of 3.6 kJ/mol. The best-fit line is $y = -234 + 0.97x$, but its standard deviation is 3.5 kJ/mol, not significantly better.

These three adsorbates are each thought to bind to the Pt(111) surface through a single σ bond to a single Pt atom (i.e., on an atop site),^{10,16–18} which is similar to the bonding picture for a ligand bound with a single σ bond to the metal center in the organometallic complexes of the correlation reported by Bryndza and co-workers.^{1,11,15} Thus, the reason this trend in Figure 1 holds must be the same reason why this trend also holds for organometallic complexes.^{1–3} To our knowledge, no physical explanation has been published to explain that trend.

We offer the following simple explanation for Figure 1. To a first approximation, the orbitals involved in the O–Pt bond are identical in local character for all three adsorbates, at least with respect to their average nuclear–nuclear, electron–nuclear, and electron–electron Coulomb potential energies and quantum-mechanical electron kinetic energies. These are only mildly affected by the next neighbor to the O atom. The main difference in adiabatic bond dissociation energies is therefore due to final-state effects (i.e., differences in the way this orbital rearranges in the dissociated products). Since the fragment-free Pt surface is one product, but the same in all three cases, the

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Table 1. Calorimetrically Measured Standard Heats of Formation (ΔH_f°) and Adsorbate–Pt(111) Bond Strengths (i.e., Adiabatic Bond Enthalpies) of Three Oxygen-Bound Adsorbates on Pt(111) and Their Corresponding Gas-Phase RO–H Bond Strengths^a

adsorbate	ΔH_f° (kJ/mol)	bond enthalpy (kJ/mol)	
		known for RO–H	measured for RO–Pt(111)
-OD	-210 ± 7^{13}	500 ⁵	$248 \pm 7^{10,13}$
-O(O)CH	-353 ± 10^{11}	469 ± 13^{14}	224 ± 13^{11}
-OCH ₃	-170 ± 10^{12}	437 ¹⁵	187 ± 11^{12}

^aLiterature citations are given as superscripts to the enthalpy values.

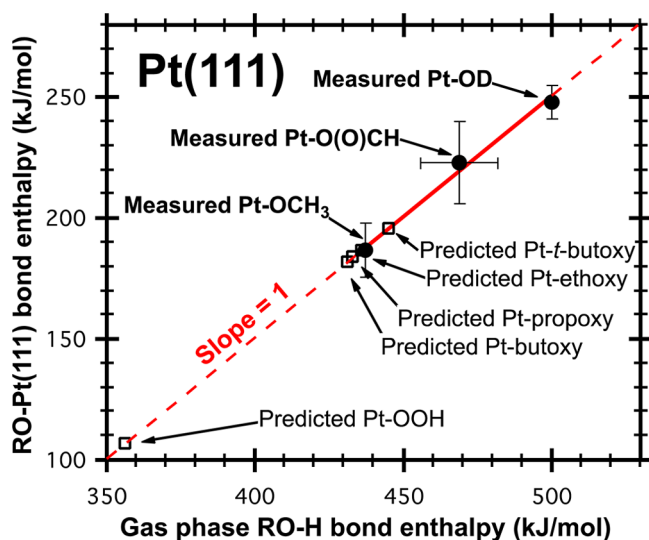


Figure 1. Calorimetric adiabatic bond dissociation enthalpies of three oxygen-bound adsorbates (deuterated hydroxyl, methoxy, and monodentate formate) to Pt(111) (●) versus their corresponding gas-phase hydrogen–OR adiabatic bond dissociation enthalpies. A line with slope equal to 1.00 fits these three points nearly perfectly. This allows the prediction of the bond strength of other important oxygen-bound adsorbates on Pt(111) that have not been measured (□), such as other alkoxy species and hydroperoxy. The error bars on each measurement represent 95% confidence limits.

only difference between these fragments is their ability to stabilize the gaseous radical that is produced upon homolytic bond cleavage. For example, methoxy stabilizes this radical much better than hydroxyl, since it has more atoms and greater structural and orbital flexibility to stabilize the radical's electron. This is the very same reason the CH₃O–H bond is weaker than the HO–H bond in the corresponding gas-phase molecules. This is why the RO–Pt(111) bond energy tracks the corresponding RO–H bond energy with a slope of unity: the differences in these dissociated final states between these three different -OR species are the same whether cleaving the RO–H

or RO–Pt(111) bond. This trend highlights the local character of the σ bond of molecular fragments to metal surface atoms, even on extended metal surfaces. The local nature of bonds to metal surfaces is apparent in the reasonable success of the bond order conservation method in predicting adsorbate energies.^{19,20}

The fitted line in Figure 1 allows the bond enthalpy of several other oxygen-bound adsorbates to be predicted (approximately). In Table 2, the predicted bond enthalpies of several alkoxy fragments and the hydroperoxy species to the Pt(111) surface are listed along with their corresponding known gas-phase hydrogen–ligand bond strengths. Also listed are the adsorbates' predicted heats of formation, which are found by summing the heat of formation of the gas-phase radical with the negative of the predicted bond enthalpy. To calculate the heat of formation of the alkoxy radicals, the known bond dissociation enthalpy (Table 2, column 3) was used with the known heats of formation of the gaseous alcohols (also listed)^{4,21} and with the known heat of formation of gas-phase H atoms (218 kJ/mol⁴).

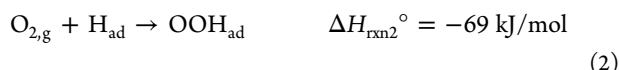
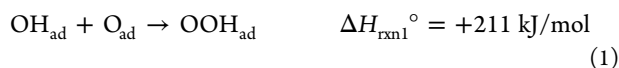
From these predicted values, insight can be gained into the thermodynamics of a wide variety of chemical pathways on Pt(111). As an example, let us focus on the hydroperoxy species (OOH_{ad}), whose standard enthalpy of formation ($\Delta H_f^\circ(\text{OOH}_{ad})$) can be predicted from this trend (Table 2, column 5), as described above. Note that the predicted bond enthalpy of OOH_{ad} to Pt(111) is 107 kJ/mol, close to what has been calculated by DFT (99.7 kJ/mol).¹⁸ This adsorbate has relevance in polymer electrolyte membrane fuel cells, where the oxygen reduction reaction occurs over a Pt-based catalyst, but during this reaction hydrogen peroxide is formed as an unwanted byproduct that degrades the membrane. Two chemical pathways have been proposed to form the hydroperoxy intermediate (reactions 1 and 2 below), whose reaction enthalpies can be calculated on Pt(111) from the empirical heats of formation of OH_{ad}^{10,13} and O_{ad}¹³ and the predicted OOH energetics in Table 2. Using this predicted $\Delta H_f^\circ(\text{OOH}_{ad})$ of -105 kJ/mol with the standard heats of

Table 2. Predicted Heats of Formation and Bond Enthalpies of Several Oxygen-Bound Adsorbates on Pt(111) from the Fitted Line in Figure 1^a

adsorbate	bond enthalpy (kJ/mol)		ΔH_f° (kJ/mol)	
	known for RO–H	predicted for RO–Pt(111)	known for gaseous alcohol	predicted for adsorbate
<i>tert</i> -butoxy	445 ²⁶	196	-313^{21}	-282
ethoxy	436 ⁵	187	-234^4	-203
propoxy	433 ⁵	184	-256^4	-225
butoxy	431 ⁵	182	-277^4	-246
OOH ^b	356 ⁴	107	-136^4	-105

^aLiterature citations are given as superscripts to the known enthalpy values. ^bOOH = hydroperoxy.

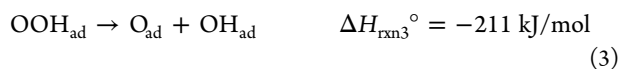
formation of OH_{ad} , O_{ad} , and H_{ad} measured on $\text{Pt}(111)^{10,13,22,23}$ allows the following reaction enthalpies to be estimated:



From the reaction enthalpies associated with reactions 1 and 2, it is clear that the most energetically favorable route to form OOH_{ad} is through reaction 2, which is the insertion of O_2 into an adsorbed hydrogen adatom to form the OOH_{ad} species (with the O_2 probably weakly adsorbed first).

A spectroscopic study by MacNaughton et al.²⁴ seems to be consistent with the thermodynamics of the above reactions, finding that H_{ad} promotes the formation of the OOH_{ad} species on $\text{Pt}(111)$. This O_2 insertion into the metal–H bond is also the same mechanism observed for making the -OOH ligand on a Pd organometallic complex.²⁵

Another interesting insight from these reaction enthalpies comes from the reverse of reaction 1, or the decomposition of an OOH_{ad} to OH_{ad} and O_{ad} :



The sum of reactions 2 and 3 provides a stepwise-exothermic route to form O_{ad} and OH_{ad} from O_2 on H-covered surfaces which are key intermediates for many reactions, although kinetics may prevent this path.

Based on the reason for the slope of 1.00 in Figure 1 offered above, it is very likely that this trend also holds for adsorbate species that are bound to the surface through other elements like carbon, as also suggested by DFT but with different slope.^{8,9} However, because $\text{Pt}(111)$ could tend to bond to carbon more strongly than oxygen, or vice versa, it may be that the corresponding line for C still retains a slope equal to 1.00 but is shifted to higher or lower ligand–metal bond strengths (i.e., larger or smaller y -intercept) than the line for these oxygen-bound species. Surprisingly, our measured value for the C– $\text{Pt}(111)$ bond enthalpy for adsorbed methyl ($-\text{CH}_3$) of 197 kJ/mol locates it at the point (440 kJ/mol, 197 kJ/mol),^{4,27,28} which is only 6 kJ/mol above the line in Figure 1 for O-bound species. We have no explanation for the proximity of this C-bound species to the line for O-bound species on $\text{Pt}(111)$, but we expect this to depend on the metal. For example, Cu probably bonds to -OR groups more strongly and to $-\text{CR}_3$ groups more weakly than Pt. Interestingly, C-bound ligands in organometallic complexes lie nearly on top of the line for O-bound species.^{1,2} We found that CO_{ad} does not fall near the line in Figure 1, but this was expected since the adsorbates in Figure 1 bond to the metal surface through a simple σ bond like their bond to H, whereas CO bonding to Pt involves π back-bonding not possible with an H atom.

This same line in Figure 1 for $\text{Pt}(111)$ adsorbates is not expected to apply to other metal surfaces, since other metals can be more oxophilic, like copper, or less oxophilic, like gold. It is expected that the line may shift up or down significantly but keep the same slope of 1.00. Indeed, for organometallic complexes it was found that different metals could be fit to the same line if simply corrected for the differences in their bond energies to the -OH “reference” ligand,^{1,29} so we predict a similar result for metal surfaces as well. Methods for adjusting

such a trend to other metal surfaces and other sites have been suggested⁹ based on scaling relationships derived from DFT.³⁰

Unfortunately, there are some important limitations to the predictive ability of this trend. For adsorbates that form multiple bonds to the surface (like bidentate formate¹¹ or methylidyne²⁷) this trend may not hold, because of the influence of one bond on the other. Additionally, it is unlikely that this relationship can predict the energetics of large molecules that have a strong van der Waals attraction with the surface or steric repulsion, since this trend is only good for predicting the chemical bond strength between a single atom in the adsorbate and the surface. However, van der Waals corrections should be easy to estimate.

The excellent correlation found here between bond strengths to a metal surface and the corresponding bond strengths to a H atom for oxygen-bound species on $\text{Pt}(111)$ yields insight into the bonding mechanism and energetics of many adsorbates and surface reactions. This trend suggests that a combined theoretical/experimental approach could provide a fast way of estimating bond energies for adsorbates on surfaces. Since bond energies to H within gas-phase molecules are already known or easy to calculate with high accuracy, these could be used to estimate the bond energies of the corresponding molecular fragment to metal surfaces by recognizing the slope of 1.00 and knowing only one experimental point on a plot like Figure 1 for that metal surface site. This estimate would need to be corrected for larger molecular fragments with significant van der Waals attractions or steric repulsions, but estimating these corrections theoretically may prove to be more accurate and is surely far faster than quantum-mechanical calculations of the full adsorbate/substrate system.

In conclusion, the strength of σ bonds of oxygen-bound molecular fragments [$-\text{OH}$, $-\text{OCH}_3$, $-\text{O}(\text{O})\text{CH}$] to $\text{Pt}(111)$ varies linearly with the strength of binding of those same fragments to H atoms in gas-phase molecules with a slope of 1.00, but offset by -249 kJ/mol (weaker to Pt than H). This implies that the bonds to the surface are highly local in character, and suggests semiempirical methods for estimating the heats of formation of adsorbates on metal surfaces that rely on this trend.

AUTHOR INFORMATION

Corresponding Author

campbell@chem.washington.edu

Present Address

[†]E.M.K.: National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401

Notes

The authors declare no competing financial interest.

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