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Identification of General Linear Relationships between Activation Energies and Enthalpy Changes for Dissociation Reactions at Surfaces

Angelos Michaelides,[†] Z.-P. Liu,[‡] C. J. Zhang,[‡] Ali Alavi,[†] David A. King,*,[†] and P. Hu[‡]

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK, and School of Chemistry, The Queen's University of Belfast, Belfast, BT9 5AG, UK

Received June 19, 2002; E-mail: daksec@ch.cam.ac.uk

Heterogeneous catalysis plays an important role in modern society. More than 90% of the industrial scale production of chemicals proceeds with the aid of a solid catalyst and consists of elementary reactions at catalytic surfaces.[1] The key parameter that controls the rate of each elementary reaction step is the activation energy. Thanks to recent computational and methodological advances, it is now possible to determine activation energies and reaction pathways for elementary catalytic reactions from first principles.[2] Here we present evidence for, and explain the presence of, clear relationships between activation energies and enthalpy changes of dissociation reactions in heterogeneous catalysis.

Calculations have been performed within the plane−wave pseudopotential formalism of density functional theory (DFT).[3] With this approach we have determined transition and final state geometries and energies for an extensive set of reactions on a variety of late transition metal surfaces. A complete list of the more than 50 elementary steps investigated, along with their associated activation energies and enthalpy changes (ΔH), can be found in the Supporting Information. The investigated reactions include adsorbate dehydrogenation (hydrogenation), CO_2 dissociation (CO oxidation), hydrocarbon cracking (coupling), and a variety of diatomic dissociation reactions. Clearly, this is a large set of reactions and encompasses specific examples or analogues of most of the key types of elementary reaction in heterogeneous catalysis. For the interested reader, further details on the typical calculation setup can be found elsewhere.[4]

Figure 1a reveals that for every reaction investigated a linear relationship exists between activation energy (E_a^{diss}) and ΔH for dissociative adsorption.[5] Behavior such as this is most often known as Brønsted−Evans−Polanyi (BEP) behavior or when considered in terms of Gibbs' free energies as linear-free-energy relationships.[6,7] It has long been believed that BEP relationships may apply to reactions in heterogeneous catalysis. Indeed considerable evidence has been provided from experiment[8−10] and from recent theoretical studies[11,12] for specific reaction systems. However, a traditional difficulty with empirical relationships of this sort is knowing what types of reaction conform. Significantly, Figure 1a reveals that a relationship between E_a^{diss} and ΔH holds for a remarkably large database of catalytic dissociation steps.[13] Moreover, we see that to a first order all dissociation reactions within the range of enthalpy changes investigated (>11 eV) fall on the same line. Since, experimentally, heats of adsorption are more accessible than activation energies, the true utility of this relationship is the estimation of reaction barriers, based purely on knowledge of adsorption energies.

Having identified a BEP line for elementary dissociation reactions at surfaces, we go further and refine this relationship: Distinct from the average BEP line (Figure 1a), the following discrete BEP lines, corresponding to particular subclasses of reaction, have been resolved (Figure 1b−d).

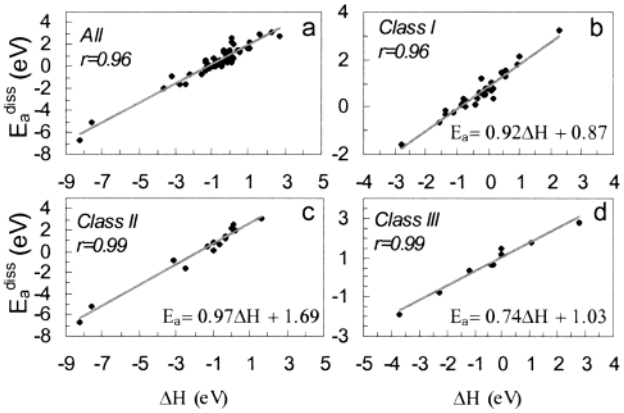

Figure 1. Plots of activation energy (E_a^{diss}) against enthalpy change (ΔH) for (a) more than 50 elementary reaction steps; (b)−(d) discrete adsorbate dehydrogenation (class I) (b); diatomic dissociation and hydrocarbon cracking (class II) (c); and triatomic dissociation (class III) (d) subclasses. The correlation coefficients (r) have been determined from linear regression analysis.

Class I: Dehydrogenation. Into this class fall all the adsorbate dehydrogenation reactions, for example O−H cleavage in H_2O or C−H cleavage in CH_x fragments. The fundamental BEP relationship that we identify for this class of reaction (in eV) is

$$E_a^{diss} = (0.92 \pm 0.05)\Delta H + 0.87 \pm 0.05 \qquad (1)$$

Class II: Diatomic Activation and Hydrocarbon Cracking. A second distinct BEP line has been resolved for "diatomic activation" and hydrocarbon cracking reactions. Diatomic activation involves the dissociation of stable diatomic molecules such as N_2 and O_2 and is a prerequisite to many catalytic processes. Hydrocarbon cracking reactions involve C−C bond cleavage, for example, C−C bond breaking in C_2H_4. This class of reactions is characterized by

$$E_a^{diss} = (0.97 \pm 0.05)\Delta H + 1.69 \pm 0.15 \qquad (2)$$

Thus, within the enthalpy range investigated, these molecules are inherently more difficult to activate than the molecules in class I: For a given ΔH a higher E_a^{diss} is encountered. This corresponds to an upward displacement of the class II BEP line relative to the class I line (Figure 2).

Class III: Triatomic Activation. This class comprises mainly CO_2 but also similar doubly bonded triatomic molecules such as NO_2 and N_2O. We find that although these reactions still sit comfortably on the average BEP line, their dependence on ΔH (slope) relative to class I and II reactions has been reduced:

[†] University of Cambridge.
[‡] The Queen's University of Belfast.

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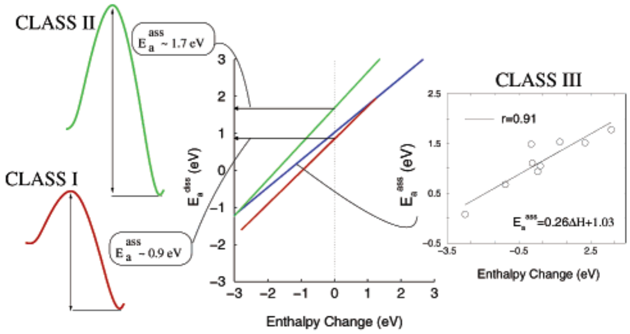

Figure 2. A schematic diagram illustrating the relationship between the three discrete Brønsted−Evans−Polanyi lines identified and their corresponding reverse association activation energies.

$$E_a^{\text{diss}} = (0.74 \pm 0.05)\Delta H + 1.03 \pm 0.08 \qquad (3)$$

Clearly, it is important to understand why these relationships hold and why discrete BEP lines exist. From the principle of microscopic reversibility, the quantity that links the activation energy with ΔH for a dissociation reaction is the activation energy of the reverse association reaction (E_a^{ass}):[1]

$$E_a^{\text{diss}} = E_a^{\text{ass}} + \Delta H \qquad (4)$$

After careful examination of all the association activation energies, we find that these lie at the origin of the observed trends. First, with regard to the overall general relationship, we see that E_a^{ass} changes much less with ΔH than E_a^{diss} does. The maximum variation of E_a^{ass} is about 2 eV, while for E_a^{diss} it is nearly 10 eV. It is for this reason that all the dissociation barriers can be fitted on to a single line with a slope close to 1 (0.86), rather than the classical value of 0.5.[6b] Indeed, the slope close to unity identified here implies that surface dissociation reactions tend to access product-like or "late" transition states. Second, considering the discrete variations of each class of reactions, we see that the specific value of E_a^{ass} can be quite different for the different classes. For class I reactions, the average E_a^{ass} is 0.9 eV, while for class II reactions it is 1.7 eV. In fact, this is the major difference between these two classes. They both possess high slopes (0.92 and 0.97 for class I and II, respectively) but have quite different intercepts (the intercept is the average E_a^{ass} if the slope is 1[14]). Finally, there is a quite good linear relationship between E_a^{ass} and ΔH for class III reactions, shown as an inset in Figure 2, while the slopes for class I and class II association reactions are very small (<0.1). This explains why the E_a^{diss} slope of class III is smaller than those of class I and class II. A schematic diagram illustrating the relationship between the BEP lines in classes I−III is shown in Figure 2.

Having seen that the existence of distinct BEP lines is related to distinct trends in the reverse association barriers, we now discuss the physical origin of the association reaction barriers in each class of reaction. The association barriers have been decomposed into two broad contributions:

$$E_a^{\text{ass}} = E_{\text{trans}} + E_{\text{int}} \qquad (5)$$

where E_{trans} is the sum of the energy incurred upon bringing both reactants from their initial states to their transition state positions in the absence of the other reactant. E_{int} is the difference between E_a^{ass} and E_{trans} and accounts for any repulsive interactions between adsorbates at transition states.[15]

This DFT decomposition analysis has been performed on representative sets of reactions on different metals in each class. This reveals that when attempting to distinguish between discrete BEP lines an important factor to consider is the transition state structure. The transition states in class III are similar and in general distinct from those in the other classes in that the reactants *do not* share direct bonding with any of the same metal atoms (Supporting Information, Figure S1). In this case one would expect that E_{int} in (5) would be small. After decomposing each of the CO oxidation activation energies in class III, we see that E_{int} is negligible, always less than 0.1 eV. Class III activation energies can, therefore, be approximated by E_{trans} ($E_a^{\text{ass}} \sim E_{\text{trans}}$). In many instances, E_{trans} is correlated to the adsorption energy.[11] Since, in addition, the adsorption energy is simply related to the ΔH, we find a clear variation of E_{trans}, and hence E_a^{ass}, with ΔH (Figure 2). In the transition states of the C + H and C + O reactions (classes I and II), however, the adsorbates *do* share bonding with a metal atom. In this case one would expect E_{int} (which does not depend on adsorption energy[16]) to be a greater component of the reaction barrier than in the class III reactions. Indeed, we find, for the specific cases of the C + H and C + O reactions, that E_{int} contributes on average 59% and 64%, respectively, of the reaction barriers. Moreover, it is in the E_{int} term that the main distinction between class I and class II reactions arises. The mean E_{int} for the C + O and C + H reactions, for example, is 1.13 and 0.51 eV, respectively. Thus we see that mostly because of an increased repulsion at the transition states class II reactions have larger association barriers than class I reactions.

Several well-resolved BEP relationships exist for elementary surface reactions. As a result, it may be possible to estimate activation energies for elementary reactions in heterogeneous catalysis merely from information on adsorption energies.

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Supporting Information Available: A table of the activation energies and enthalpy changes of every reaction investigated as well as a supplementary figure, S-Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) E_a^{diss} and ΔH are always referenced to stable molecules in the gas phase. Therefore, for CH_x, NH_x, OH_x, and SH_x intermediates all energies are relative to their saturated parent molecule, namely, CH_4, NH_3, H_2O, and H_2S, respectively.
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(13) It is plausible that analogous relationships exist between free energies of activation and free energies of reaction for surface dissociation reactions. See, for example, ref 7 or ref 1.
(14) The slope of the E_a^{diss} against ΔH line for a class of reactions is 1 minus the slope of the corresponding E_a^{ass} against ΔH line. Thus, as the dependence of E_a^{diss} on ΔH decreases the dependence of E_a^{ass} on ΔH increases.
(15) This term includes adsorbate−adsorbate dipole−dipole interactions, Pauli repulsions, and the indirect surface mediated repulsion that occurs when reactants in close proximity share bonding with substrate atoms.
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