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. 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. 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). 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 adsorbate dehydrogenation (hydrogenation), CO2 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.

Figure 1a reveals that for every reaction investigated a linear relationship exists between activation energy ($E_a$) and $\Delta H$ for dissociative adsorption. 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. It has long been believed that BEP relationships may apply to reactions in heterogeneous catalysis. Indeed considerable evidence has been provided from experiment and from recent theoretical studies for specific reaction systems. However, a traditional difficulty with empirical relationships of this sort is knowing what holds for a remarkably large database of catalytic dissociation steps. 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).

- **Class I: Dehydrogenation.** Into this class falls all the adsorbate dehydrogenation reactions, for example $\text{O} \rightarrow \text{H}$ cleavage in $\text{H}_2\text{O}$ or $\text{C} \rightarrow \text{H}$ cleavage in $\text{CH}_4$, fragments. The fundamental BEP relationship that we identify for this class of reaction (in eV) is

$$E_a = (0.92 \pm 0.05)\Delta H + 0.87 \pm 0.05$$

- **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 $\text{N}_2$ and $\text{O}_2$ and is a prerequisite to many catalytic processes. Hydrocarbon cracking reactions involve $\text{C} \rightarrow \text{C}$ bond breaking in $\text{C}_2\text{H}_4$. This class of reactions is characterized by

$$E_a = (0.97 \pm 0.05)\Delta H + 1.69 \pm 0.15$$

Thus, within the enthalpy range investigated, these molecules are inherently more difficult to activate than the molecules in class I: For a given $\Delta H$ a higher $E_a$ 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 $\text{CO}_2$ but also similar doubly bonded triatomic molecules such as $\text{NO}_2$ and $\text{N}_2\text{O}$. We find that although these reactions still sit comfortably on the average BEP line, their dependence on $\Delta H$ (slope) relative to class I and II reactions has been reduced:

$$E_a = (0.92 \pm 0.05)\Delta H + 0.87 \pm 0.05$$

**References:**

1. University of Cambridge.
2. The Queen’s University of Belfast.

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of the reverse association reaction (\(E_{a}^{\text{ass}}\)) (10). After decomposition of each of the CO oxidation activation energies in class III, we see that \(E_{a}^{\text{ass}}\) is negligible, always less than 0.1 eV. Class III activation energies can, therefore, be approximated by \(E_{a}^{\text{trans}}\) (\(E_{a}^{\text{ass}} \approx E_{a}^{\text{trans}}\)). In many instances, \(E_{a}^{\text{trans}}\) is correlated to the adsorption energy. (11) Since, in addition, the adsorption energy is simply related to the \(\Delta H\) for a clear variation of \(E_{a}^{\text{trans}}\), and hence \(E_{a}^{\text{ass}}\), with \(\Delta H\) (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 \(E_{a}^{\text{int}}\) (which does not depend on adsorption energy) 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 \(E_{a}^{\text{int}}\) contributes on average 59% and 64%, respectively, of the reaction barriers.

Moreover, it is in the \(E_{a}^{\text{int}}\) term that the main distinction between class I and class II reactions arises. The mean \(E_{a}^{\text{int}}\) 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.

References

(5) \(E_{\text{ass}}\) and \(\Delta H\) are always referenced to stable molecules in the gas phase.
(6) Therefore, for \(\text{CH}_2\), \(\text{NH}_3\), \(\text{H}_2\text{O}\), and \(\text{H}_2\text{S}\), respectively.
(15) 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.

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