FEATURE ARTICLE

The Influence of Catalytic Surfaces on the Barriers to Elementary Surface Reaction Steps

Andrew J. Gellman*

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Received: August 8, 2001; In Final Form: June 14, 2002

The transition states to elementary reaction steps on surfaces have received little attention because of the lack of experimental probes of their structure and properties. This lack of understanding of the transition states for surface reactions places severe constraints on our ability to predict the kinetics of catalytic reactions and other surface chemical processes. The use of substituent effects has provided one approach to probe the nature of transition states and a means for determining whether such transition states can be considered to occur early or late in the reaction coordinate. This has been applied to several well-defined elementary surface reactions. As examples, the transition state for β-hydride elimination in adsorbed alkyl and alkoxy groups is believed to occur late in the reaction coordinate while the transition state for dehalogenation reactions on surfaces is believed to occur early in the reaction coordinate. Combining this knowledge with a comprehensive review of the barriers to these reactions on a wide variety of surfaces has suggested a simple proposition for considering the effects of surfaces on the barriers to elementary reactions. The barriers to elementary reaction steps with *late* transition states are expected to be sensitive to the nature of the surface while the barriers to reactions with *early* transition states are expected to be relatively insensitive to the nature of the surface. This proposition is illustrated by first considering the trivial examples of molecular adsorption and desorption on surfaces and then by discussion of surface activated β-hydride elimination and dehalogenation reactions.

1. Introduction

Catalysis science is fundamentally a science of kinetics. At the heart of any catalytic process is the reaction mechanism, a complex network of elementary reaction steps leading from reactants to both desired and undesired products. Much of catalysis science is devoted to the acceleration of reaction rates and to the control of selectivity among competing reaction pathways. This is primarily an exercise in understanding and controlling reaction kinetics and, in particular, controlling the rate constants of the many elementary steps that make up the overall reaction mechanism. The quantities which predominantly determine the values of the rate constants are their activation barriers $\Delta E^{\ddagger}$, the differences in zero-point energies between the reactants, and the transition states for each elementary step. While a great deal of effort in the field of surface science has focused on the characterization of the stable intermediates that are the reactants and products of each elementary step, very little work has addressed the nature of the transition states for these elementary steps that dictate overall reaction rates.[1-6] Ultimately, this is critical to the development of catalysis science since the control of catalytic processes requires an understanding of the influences of catalytic surfaces on the values of the $\Delta E^{\ddagger}$ for each elementary reaction step. This article articulates a simple proposition for the influence of a catalytic surface on the $\Delta E^{\ddagger}$ to elementary surface reaction steps that can be classified as having transition states that occur either early or late in the reaction coordinate.

The development of transition state theory by Eyring and Polanyi in 1935 provided a simple relationship between the rate

* To whom correspondence should be addressed. E-mail: ag4b@andrew.cmu.edu.

constant for an elementary reaction and the properties of the reactant and the transition state.[7,8] It did not, however, provide any means for thinking about the characteristics of the transition state other than through the analysis of a potential energy surface (PES) that must be determined by other means. A commonly used conceptual framework for thinking about the nature of transition states is to classify them as either reactant-like, if they occur early in a reaction coordinate, or product-like, if they occur late in the reaction coordinate. It should be kept in mind that there are undoubtedly many examples of surface reactions for which the transition state cannot realistically be categorized so simply. Nonetheless, the fact that the transition states to some types of reactions can be considered to be either reactant-like or product-like can be a useful starting point for thinking about their properties and the influence of surfaces on their properties. A simple framework for thinking about the role or effect of surfaces on the transition states and the $\Delta E^{\ddagger}$ to elementary reaction steps does not exist but could be a useful tool in the further development of catalysis science.

There are a limited number of approaches to the study of the transition states to elementary surface reactions and as a result a very limited body of knowledge concerning their properties and characteristics. The use of state resolved molecular beam methods and their counterpart, state resolved desorption methods, have provided the bulk of the experimental data on the dynamics of adsorption and desorption processes.[9–11] Examples include studies of methane, nitrogen, and hydrogen dissociation on metals such as Cu(111), Ru(001), Ir(110), and Pt(110). Computational theory is probably the fastest growing contributor to the description of transition states for surface reactions. Although computational methods are limited in their ability to predict the kinetics of surface reactions accurately and consistently, they do provide transition state structures that seem to be internally consistent.[12,13] Of course, it is usually the $\Delta E^{\ddagger}$ and the kinetics to surface reactions that have been measured experimentally and that provide the benchmarks for such computational descriptions. Unfortunately, theoretical methods provide descriptions of both the atomic structure and the electronic structure of transition states on surfaces that are well beyond any level of detail that is available experimentally. A third approach to the problem has been the use of substituent effects to probe surface transition states.[5,6] By measuring the kinetics of elementary surface reactions using reactants with a range of substituents it is possible to measure the effects of the substituent on the $\Delta E^{\ddagger}$. As an example, the substitution of fluorine into the methyl group of ethoxy species (RCH$_2$O−, R = CH$_3$ or CF$_3$) adsorbed on the Cu(111) surface results in an increase of 15 kcal/mol in the $\Delta E^{\ddagger}$ for β-hydrogen elimination.[14,15] The substituent field will interact with the electron distributions in the reactant and transition state to an elementary step to influence their relative energies and thus the barrier to reaction. As will be discussed below these substituent effects can be used to gain insight into the nature of the transition states for a number of surface reactions.

Although the sum total of our knowledge of transition states on surfaces is not great, it has reached the point that it is possible to consider general relationships between the nature of these transition states and the influence of the catalytic surface on the $\Delta E^{\ddagger}$ for different types of surface reactions. The role of this article is to review the state of our knowledge of a few surface reactions for which a large number of kinetic measurements have been made and for which we have some insight into the nature of the transition state. The goal is to articulate a simple proposition that suggests a relationship between the
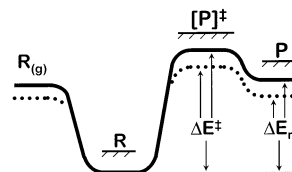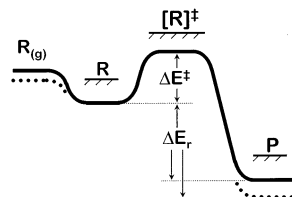
Figure 1. One-dimensional PES's that illustrate the effects of catalysts on reactions with early and late transition states. The top PES's illustrate a process in which a gas-phase reactant, R$_{(g)}$, adsorbs onto the surface to form the adsorbed species R which then reacts to form a reaction product, P, on the surface. The transition state for this surface reaction [P]‡ occurs late in the reaction coordinate and thus is product-like. The solid and dashed lines represent the PES's for this reaction on two different catalytic surfaces. The nature of the surface will influence the relative energies of the reactant and product ΔE_r, and since the transition state is product-like it will also influence the reaction barrier $\Delta E^{\ddagger}$. The lower PES's represent a reaction with an early or reactant-like transition state, [R]‡, on two different surfaces. Although the nature of the surfaces still influences the value of ΔE_r, the fact that the transition state is reactant-like means that the difference in the surfaces has relatively little effect on the $\Delta E^{\ddagger}$.

nature of the transition state and the effects of changes to the surface on the $\Delta E^{\ddagger}$ to that reaction. This proposition will serve as a framework for the discussion of the surface reactions for which the nature of the transition state is known. Simply put the proposition is as follows:

1. The $\Delta E^{\ddagger}$ to elementary reactions with *late* transition states should be *sensitive* to the nature of the catalyst surface and to changes in the surface.

2. The $\Delta E^{\ddagger}$ to elementary reactions with *early* transition states should be relatively *insensitive* to the nature of the catalyst surface and to changes in the surface. In this context the "nature" of the surface can refer to both composition and structure. Changes to the nature of the surface would be those that perturb the reaction energetics but not to the extent that they completely change a reaction mechanism or change the nature of the transition state to an elementary step of interest. The rationale behind this proposition is quite simple and is illustrated in Figure 1. The figure shows two sets of one-dimensional PES's for a surface reaction in which a reactant R$_{(g)}$ adsorbs on a substrate surface as R and then undergoes a reaction to form the adsorbed product P. In the upper part of Figure 1 the reaction of R to P occurs via a late transition state, which is depicted as being product-like, [P]‡. The figure shows two PES's, the solid and the dotted lines, which describe the energetics of the reaction on two different surfaces. Both PES's are referenced to the energy of the adsorbed reactant R. Changes in the surface will influence the relative energies of the reactant and the product and thus change the reaction energy, ΔE_r. If the transition state is product-like, then one would also expect changes in the surface to influence the reaction barrier $\Delta E^{\ddagger}$. Thus, for the reaction with the *late* transition state, the $\Delta E^{\ddagger}$ is *sensitive* to the nature of the surface. The lower half of Figure 1 illustrates

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the opposite extreme, a reaction in which the transition state occurs early in the reaction coordinate and is reactant-like, $[R]^{\ddagger}$. Once again the PES's are shown using the solid and the dotted lines for the same reaction occurring on two different surfaces. In this case one still expects a change in the surface to influence the reaction energy ΔE_r; however, because the transition state is reactant-like, these changes should have little effect on the relative energies of the reactant and transition state and thus little influence on the $\Delta E^{\ddagger}$. Thus for a reaction with an *early* transition state the $\Delta E^{\ddagger}$ is relatively *insensitive* to the nature of the surface. In reality one cannot expect the $\Delta E^{\ddagger}$ to reactions with early transition states to be completely insensitive to changes in the surface. However, on the basis of the arguments made above, the $\Delta E^{\ddagger}$ to reactions with late transition states should be far more sensitive to changes in the nature of the surface than the $\Delta E^{\ddagger}$ to reactions with early transition states. Note that this proposition does not try to suggest how one goes about determining whether the transition state to a particular elementary surface reaction can be considered reactant-like or product-like. It merely tries to delineate the consequences for those elementary steps with transition states that can be legitimately considered to have transition states that are either reactant-like or product-like.

This article will begin by discussion of two types of reactions that serve as trivial cases to illustrate this proposition: molecular adsorption and molecular desorption from surfaces. This is followed by discussions of surface reactions with early and late transition states: dehalogenation on the Ag(111) and Pd(111) surfaces and β-hydride elimination on the Cu(111) surface. Finally, a comprehensive survey of the measured values of the $\Delta E^{\ddagger}$ to these reactions on a wide range of surfaces is presented in support of the proposition articulated above.

2. Case I: Molecular Adsorption

Molecular adsorption is a simple surface process that can be used to illustrate the application of the proposition to a reaction with an early transition state. Molecular adsorption is always exothermic and is usually believed to occur with little or no barrier, $\Delta E^{\ddagger} \approx 0$. As such the transition state must be considered to occur early in the reaction coordinate and to be reactant-like. The usual measure of the kinetics of adsorption is the sticking coefficient S_0, which should be measured under conditions where the rate of desorption is negligible. This usually means low temperature. Under these conditions the sticking coefficients of most molecules (at thermal energies) on most surfaces is of order $S_0 \approx 1$ and almost independent of the surface on which the measurement is made.[16,17] It should be noted that even variations of the sticking coefficient in the range $0.1-1.0$ can be considered small in the context of this discussion and are negligible when compared to the possible range of values of rate constants for the majority of activated surface reactions. Thus molecular adsorption represents an extreme case in which the $\Delta E^{\ddagger}$ to reaction is insensitive to the nature of the surface.

It is important to realize that molecular adsorption reactions are not the dissociative adsorption processes that often have significant barriers and can have very low dissociative sticking coefficients. Examples of dissociative adsorption processes with low sticking coefficients would be O_2 dissociation on Ag surfaces and N_2 dissociation on Fe surface.[18−22] These types of reactions are not elementary and are more properly considered as two step processes: trapping adsorption followed by dissociation. It is usually the second step that is activated and if the $\Delta E^{\ddagger}$ to dissociation of the trapped molecule is greater than the molecular desorption energy, ΔE_{des}, the overall process of

dissociative adsorption from the gas phase will appear to have a net activation barrier.

3. Case II: Molecular Desorption

Just as molecular adsorption is always exothermic, molecular desorption is endothermic. Microscopic reversibility requires that if the transition state to molecular adsorption occurs *early* in the adsorption reaction coordinate, then the transition state to desorption must occur *late* in the desorption reaction coordinate. Furthermore, since the adsorption process is usually considered to occur with little or no $\Delta E^{\ddagger}$, this implies that the barrier to desorption $\Delta E^{\ddagger}_{des}$ is equal to the desorption energy ΔE_{des}.

$$\Delta E^{\ddagger}_{des} = \Delta E_{des}$$

The most common method for measurement of the $\Delta E^{\ddagger}_{des}$ is temperature programmed desorption (TPD). This measurement can be used for species that desorb from surfaces rather than decomposing during heating, a condition that is usually met if the ΔE_{des} is lower than the barrier to decomposition, $\Delta E^{\ddagger}_{decomp}$.

$$\Delta E_{des} < \Delta E^{\ddagger}_{decomp}$$

TPD is a fairly simple and routine measurement, and as a result, the values of $\Delta E^{\ddagger}_{des}$ have been reported for a large number of molecules adsorbed on many surfaces.

There are numerous reports of measured values of $\Delta E^{\ddagger}_{des}$ of molecules on surfaces. Not surprisingly these revealed that the $\Delta E^{\ddagger}_{des}$ of a given molecule measured on a range of different surface can vary quite widely. For example the measured desorption energies of CO from metal surfaces vary from 16 to 38 kcal/mol at low coverages.[23] In reality the range is probably even greater than this since measurements of ΔE_{des} on most surfaces that dissociate CO have not been made. Clearly molecular desorption serves as a trivial example of the first portion of proposition stated above. The transition state to desorption occurs late in the reaction coordinate for desorption and the values of $\Delta E^{\ddagger}_{des}$ for a given molecule are clearly sensitive to the nature of the surface from which it desorbs.
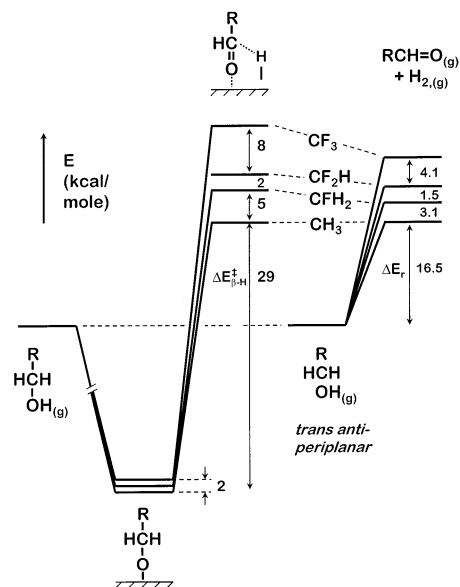
4. Case III: β-Hydride Elimination

It is particularly easy to measure the kinetics for surface reactions involving either a reactant or product that is a gas-phase species as in the cases of adsorption and desorption. The reactant and product are partitioned in space and thus it is possible to measure reaction rates by detecting either the loss of species from the gas phase or their appearance in the gas phase using mass spectrometry or some other method that is equally sensitive and fast. Thus, there have been many measurements of sticking coefficients and thermal desorption rates that have lead to the conclusions of the two sections above. By comparison, there are far fewer measurements of the kinetics of reactions for which both the reactant and product are adsorbed species. Often this requires the use of spectroscopic methods which must be able to discriminate between reactant and product and give signals that are easily related to surface concentrations. Furthermore, such methods must be relatively fast in order to allow measurements of changes in concentration over experimentally realizable time scales. Although this can be achieved and there are quite a number of measurements of surface reaction rates, there are very few classes of reactions for which the rate constants and the $\Delta E^{\ddagger}$ have been determined on a wide variety of surfaces.

β-Hydride elimination is an extremely common surface reaction of adsorbed alkyl and alkoxy groups. As illustrated below the reaction in alkoxy groups generates adsorbed aldehydes or ketones. In the case of alkyl groups, β-hydride

elimination results in the production of adsorbed primary or secondary olefins. This is a particularly common and thus important elementary step in the reactions of hydrocarbons on many surfaces and thus has been the subject of careful study.[2,24] One important aspect of the β-hydride elimination reaction is that on many surfaces the product is sufficiently weakly adsorbed that its desorption rate constant k_{des} is much higher than the reaction rate constant $k_{\beta-H}$. As a consequence, the desorption of the product is rapid and the measurement of its desorption rate into the gas phase serves as a good measure of the surface reaction rate. Thus TPD measurements can be used to measure the rates and the barriers to β-hydride elimination $\Delta E_{\beta-H}^{\ddagger}$ on many surfaces. The reaction is believed to be elementary, and thus the measured barriers are believe to reflect the properties of a simple PES with one barrier separating reactant and product. Finally, in some instances the energetics to β-hydride elimination have been measured or calculated and the reaction is found to be endothermic.[14,25,26]

The nature of the transition state for β-hydride elimination is probably better understood than that of any other hydrocarbon surface reaction. The bulk of this insight comes from the results of measurements of β-hydride elimination in alkoxides on the Cu(111) surface.[14,15] These measurements have made use of fluorine substituent effects to perturb the $\Delta E_{\beta-H}^{\ddagger}$ in ethoxides (RCH_2O-Cu, $R = CH_3$, CFH_2, CF_2H, and CF_3) and isopropanoxides ($R'RCHO-Cu$, R and $R' = CH_3$, CF_3). Fluorination increases the measured values of $\Delta E_{\beta-H}^{\ddagger}$ from 29 kcal/mol in ethoxide to 62 kcal/mol in hexafluoroisopropanoxide. Figure 2 illustrates a one-dimensional PES for β-hydride elimination in the ethoxides on the Cu(111) surface. At the left is the adsorption of the ethanols from the gas phase to produce adsorbed ethoxides which then pass through the transition state to β-hydride elimination. The effect of fluorination on the $\Delta E_{\beta-H}^{\ddagger}$ is illustrated and results in an increase by $\Delta\Delta E_{\beta-H}^{\ddagger} = 15$ kcal/mol. This large substituent effect can be understood in a number of ways. The right-hand side of Figure 1 illustrates the effect of fluorination on the energetics of the gas-phase reaction going from the ethanols to acetaldehydes. Fluorination increases the reaction energy by $\Delta E_r \approx 9$ kcal/mol. In other words a large portion of the effect of fluorination on the $\Delta E_{\beta-H}^{\ddagger}$ can be attributed to its effect on ΔE_r, suggesting that the transition state to β-hydride elimination is product-like. This is born out by a recent computational study of β-hydride elimination in methoxy groups to produce formaldehyde on the Cu(111) surface.[26] That study shows that the reaction is endothermic by $\sim$24 kcal/mol and that the transition state is product-like in the sense that the C−O bond length is 1.26 Å which is much closer to that of the product formaldehyde (1.23 Å) than it is to that of the reactant methoxy group (1.43 Å). The effect of fluorine substitution on the $\Delta E_{\beta-H}^{\ddagger}$ can also be quantified empirically using the field effect substituent constants, σ_F.[27,28] Figure 3 correlates the $\Delta E_{\beta-H}^{\ddagger}$ with the σ_F and reveals a very high value of the reaction constant, $\rho = 36 \pm 5$ kcal/mol. This value is typical


Figure 2. Potential energy diagram for the β-hydride elimination reaction in fluorinated ethoxides on the Cu(111) surface. The reference energy level at the left is the energy of the gas-phase ethanols. Formation of the adsorbed ethoxides is only weakly influence by fluorination. The activation barrier to β-hydride elimination ($\Delta E_{\beta-H}^{\ddagger}$) is increased by 15 kcal/mol by fluorination of the methyl group. At the right-hand side is the energy scale for the dehydrogenation of fluorinated ethanols in the gas phase. This is the same overall reaction as on the Cu(111) surface and the effects of fluorine on the reaction energetics (ΔE_r) for dehydrogenation map directly onto the effects of fluorine on the $\Delta E_{\beta-H}^{\ddagger}$. This suggests that the transition state to β-hydrogen elimination occurs energetically late in the reaction coordinate.

of a gas-phase ionic reaction. In the case of β-hydride elimination it can be understood quite easily in terms of a transition state in which the carbon atom is electron deficient with respect to the initial state. This is illustrated in the transition state depicted in Figure 3. It is important to point out that these substituent effects have also been observed on the Cu(100), Cu-(110), and Ag(110) surfaces.[15] All this evidence suggests that the β-hydride elimination reaction occurs with a late transition state on these surfaces.

β-Hydride elimination also occurs in alkyl groups on many metal surfaces and generates olefins as reaction products. As in the case of the alkoxides on the Cu(111) surface this reaction has been studied using fluorine substituent effects to probe the nature of the transition state.[29] On comparison of the $\Delta E_{\beta-H}^{\ddagger}$ for propyl groups ($CH_3CH_2CH_2-Cu$) and trifluoropropyl groups ($CF_3CH_2CH_2-Cu$), one finds that fluorination increases the barrier by $\Delta\Delta E_{\beta-H}^{\ddagger} = 8.4$ kcal/mol. This can be compared to computationally derived numbers for the gas-phase dehydrogenation of propane to propylene and dehydrogenation of trifluoropropane to trifluoropropylene for which fluorination increases the reaction energy by $\Delta\Delta E_r = 4.5$ kcal/mol.[14] As in the case of β-hydride elimination in the alkoxides the effect of fluorination on the ΔE_r accounts for a large fraction of its effect on the $\Delta E_{\beta-H}^{\ddagger}$. The implication is that the transition state occurs late in the reaction coordinate. This is consistent with the fact that the reaction energy for β-hydride elimination in ethyl groups on the Cu(100) surface has been measured to be endothermic by 6.5 ± 3.6 kcal/mol.[25] As in the case of β-hydride elimination in alkoxides, β-hydride elimination in alkyl groups is believed to occur with a transition state that is product-like.

β-Hydride elimination has been observed on a wide variety of surfaces. If its transition state is indeed product-like, then

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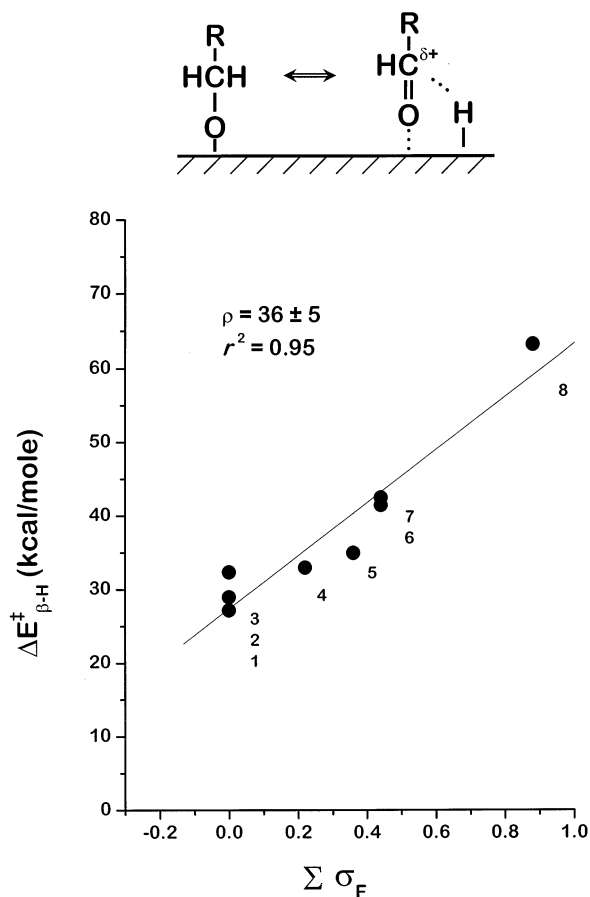
Figure 3. Activation energies for β-hydride elimination $\Delta E_{\beta-H}^{\ddagger}$ in alkoxides on Cu(111) plotted against the field substituent constants σ_F. These are defined as the sum of the field constants for the two substituent groups on the CHO reaction center. The activation barriers to β-hydrogen elimination increase with the degree of fluorination or increasing σ_F. The implication is that the β-carbon in the transition state for β-hydrogen elimination is electron deficient with respect to the initial state. **1** = $(CH_3)_2CHO_{(ad)}$, **2** = $CH_3CH_2O_{(ad)}$, **3** = $CH_3O_{(ad)}$, **4** = $CH_2FCH_2O_{(ad)}$, **5** = $CHF_2CH_2O_{(ad)}$, **6** = $(CF_3)(CH_3)CHO_{(ad)}$, **7** = $CF_3CH_2O_{(ad)}$, **8** = $(CF_3)_2CHO_{(ad)}$.

according to the proposition being put forth in this article the nature of the surface ought to have a large effect on the values of $\Delta E_{\beta-H}^{\ddagger}$ observed on these surfaces. To address this issue, the literature on this subject has been reviewed to collect all measurements of the kinetics of β-hydride elimination. The results are summarized in Figure 4 which plots the values obtained from the literature for the $\Delta E_{\beta-H}^{\ddagger}$ in ethyl (CH_3CH_2-), propyl ($CH_3CH_2CH_2-$), methoxy (CH_3O-), and ethoxy (CH_3CH_2O-) groups adsorbed on a wide range of surfaces.[30] As proposed it is quite apparent that the $\Delta E_{\beta-H}^{\ddagger}$ is sensitive to the nature of the surface and ranges from 8 to 40 kcal/mol.

Although it is not the purpose of this paper to provide a detailed review of β-hydride elimination on all the surfaces on which it has been observed, a few words about the scope of existing measurements and the methods is warranted. Ideally one would want all studies to have included spectroscopic identification of both reactant and product, deuterium labeling to clearly identify β-hydride elimination as the rate-limiting step in the kinetics, and the use of kinetics methods that would allow independent measurement of both the preexponential factor ν and the barrier $\Delta E_{\beta-H}^{\ddagger}$. Although much of this has been done on the Cu(111) surface and a very few others, the vast majority of measurements have not been so rigorous. For the most part this is simply because the study of β-hydride elimination and
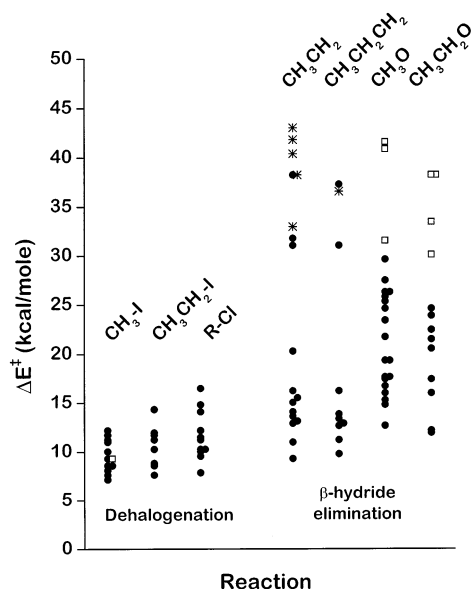
Figure 4. A summary of the $\Delta E^{\ddagger}$ to β-hydrogen elimination and dehalogenation derived from kinetics studies reported in the literature.[30] The β-hydrogen elimination reactants chosen for review were methoxy (CH_3O-), ethoxy (CH_3CH_2O-), ethyl (CH_3CH_2-), and propyl ($CH_3CH_2CH_2-$) groups. The reactants for the dehalogenation reactions were methyl iodide (CH_3I), ethyl iodide (CH_3CH_2I), and alkyl chlorides. There have been a limited number of measurements on the chlorides so, since substituents have been shown to have little effect on the barriers to the dehalogenation reactions, it is appropriate to lump all the alkyl chlorides together. The different types of surfaces used were metals (●), semiconductors (*), and metallic compounds such as oxide or carbides (□). Since very few preexponential factors have been reported in the literature the data reviewed have been analyzed assuming a common value of $\nu = 10^{13}$ s^{-1}. The primary observation to be gleaned from the compiled results is that the range of values for the $\Delta E_{\beta-H}^{\ddagger}$ is quite large, consistent with a reaction having a product-like transition state. By comparison, the barriers to dehalogenation ($\Delta E_{C-I}^{\ddagger}$ and $\Delta E_{C-Cl}^{\ddagger}$), a reaction with an early transition state, cover a relatively narrow range.

measurement of its kinetics has not been the primary objective of many of the papers in which it is reported. The majority of measurements have made use of TPD and have reported the observation of reaction products that arise from β-hydride elimination and peak desorption temperatures for the appearance of these products in the gas phase. A few measurements have made use of techniques such as vibrational spectroscopy to measure rates of reaction. Finally, only a small fraction of the reported measurements have made serious attempts to measure both the preexponent ν and the $\Delta E_{\beta-H}^{\ddagger}$ of the rate constant independently. Thus, for the purposes of reporting values of $\Delta E_{\beta-H}^{\ddagger}$ in Figure 4 it has been assumed that the preexponential factors all have a value of $\nu = 10^{13}$ s^{-1}. Although there are cases in which the preexponential factor has been measured, using a single value is deemed best for the purposes of this comparison. It should be pointed out that this assumption is not going to have any influence on the primary result to be gleaned from Figure 4, the fact that the $\Delta E_{\beta-H}^{\ddagger}$ is sensitive to the nature of the surface and has a wide range of values on the many surfaces on which it has been observed.

Finally a few words should be said about the types of surfaces that are included among those for which values of $\Delta E_{\beta-H}^{\ddagger}$ are reported in Figure 4. For the alkyl groups values of $\Delta E_{\beta-H}^{\ddagger}$ have been reported on many single-crystal metal surfaces, one metallic alloy surface, and a number of semiconductor surfaces. For the alkoxy groups values have been reported on single-crystal metals, some alloys, and several oxide surfaces. To give

the reader some insight into the sources of the numbers in Figure 4 the data points have been illustrated with solid circles for the metal surfaces, ●, open squares for the surfaces of oxides and other compounds, □, and asterisks for the semiconductor surfaces, *.[30] In many instances there have been multiple measurements on the same single crystalline surface. For the purposes of this comparison the numbers that have been reported by different laboratories have been averaged. In a number of cases measurements have been made using a single reactant such as an ethyl group adsorbed on different low Miller index surfaces of the same metal or on one surface that has been modified by the presence of coadsorbates such as oxygen atoms or sulfur atoms. A number of surface reactions are known to be structure sensitive and thus structural modifications to the surface can, in principle, influence the $\Delta E^{\ddagger}_{\beta-H}$. As a result, the values of $\Delta E^{\ddagger}_{\beta-H}$ on different low Miller index surfaces have been reported separately in Figure 4 for the purposes of this comparison. Thus the variations to the surfaces considered in Figure 4 include change of substrate material, modification by adsorbates, and changes in surface structure.

5. Case IV: Dehalogenation

The final class of reactions that will be discussed in this paper are the dehalogenation reactions and in particular the cleavage of C−Cl and C−I bonds on surfaces. Elementary dechlorination steps are of importance in a number of catalytic processes and in particular the conversion of chlorofluorocarbons (CFCs) into hydrofluorocarbons (FHCs). The cleavage of C−I bonds has been used on a wide variety of surfaces as a route to the production of alkyl groups from alkyl iodides.[2] In many instances it is the alkyl groups that are the object of investigation and the cleavage of the C−I bonds is observed incidentally. In fact many of the measurements of β-hydride elimination mentioned in section 4 have begun with the cleavage of C−I bonds in alkyl iodides to generate the alkyl precursors that then decompose by β-hydride elimination. The cleavage of C−Cl and C−I bonds has been determined to be exothermic on some metal surfaces and this is probably the case on most. Certainly in the case of the alkyl iodides, the C−I bonds are quite weak while the metal-alkyl and metal-iodine bonds that are formed as products are strong enough to render the net reaction exothermic.

There have been two studies that have attempted to probe the nature of the transition state to dehalogenation reactions on surfaces by using substituent effects. The first is a study of the dechlorination of CFCs on the Pd(111) surface.[31,32] This was motivated by the desire to probe the nature of the transition state to C−Cl cleavage which is believed to be a rate-controlling step in the overall hydrodechlorination of CFCs on Pd catalysts. The barriers to C−Cl cleavage, $\Delta E^{\ddagger}_{C-Cl}$, were determined in a set of four fluorine substituted 1,1-dichloroethanes (CF$_3$CFCl$_2$, CF$_3$CHCl$_2$, CH$_3$CFCl$_2$, and CH$_3$CHCl$_2$) on the Pd(111) surface. The values of $\Delta E^{\ddagger}_{C-Cl}$ have been scaled using the field substituent constants of the different reactants and the results are show in Figure 5. Surprisingly, the substituents have absolutely no influence on the $\Delta E^{\ddagger}_{C-Cl}$ and the reaction constant is $\rho = 0.5 \pm 1$ kcal/mol. The implication of this is that there is little change in charge density distribution between reactant and transition state and thus the fluorine substituents have little effect on the relative energetics of the reactant and the transition state. This is also consistent with a transition state to C−Cl cleavage that occurs early in the reaction coordinate and thus looks reactant-like. Such a reactant-like transition state is depicted at the top of Figure 5.
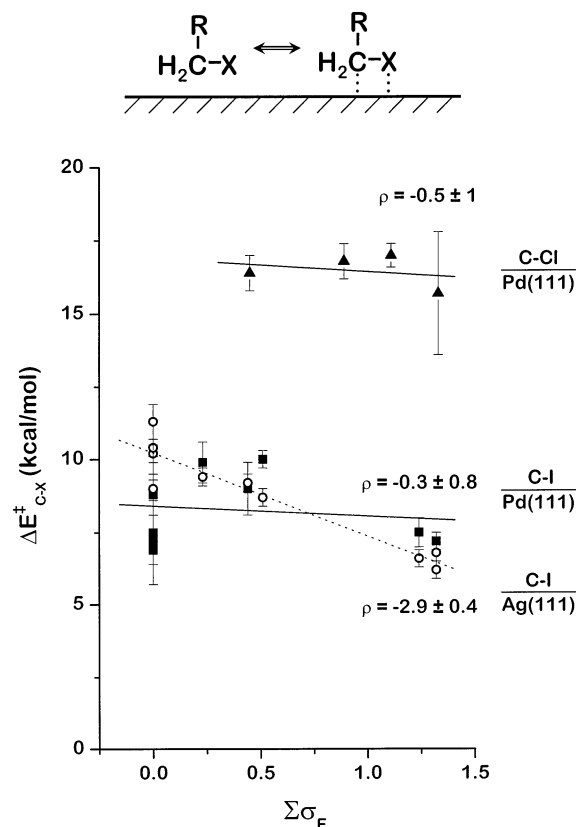
Figure 5. Activation energies for the C−Cl cleavage in 1,1-dichloroethanes on Pd(111) and for C−I cleavage in alkyl and fluoroalkyl iodides on Ag(111) and Pd(111) surfaces plotted against the field substituent constants σ_F. In all cases the reaction constant, ρ, is very small suggesting an early transition state which is reactant-like. The reactants used in the study of dechlorination were CF$_3$CFCl$_2$, CF$_3$CHCl$_2$, CH$_3$CFCl$_2$, and CH$_3$CHCl$_2$. The reactants used in the study of deiodination were R−I, R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$, CH(CH$_3$)$_2$, C(CH$_3$)$_3$, CH$_2$CF$_3$, CH$_2$CH$_2$CF$_3$, CH$_2$CF$_2$CF$_3$, CF$_3$, and CF$_2$CF$_2$H, C(CF$_3$)$_3$.

The second dehalogenation reaction that has been studied using substituent effects is the cleavage of C−I bonds on the Pd(111) and the Ag(111) surfaces.[33−35] This reaction has been studied in order to support the previously described observation that the transition state to C−Cl cleavage is reactant-like. The kinetics of C−I cleavage were measured using a set of 10 different alkyl and fluoroalkyl iodides (CH$_3$I, CF$_3$I, CH$_3$CH$_2$I, CF$_3$CH$_2$I, CF$_2$HCF$_2$I, CH$_3$CH$_2$CH$_2$I, CF$_3$CH$_2$CH$_2$I, CF$_3$CF$_2$CH$_2$I, (CH$_3$)$_2$CHI, and (CH$_3$)$_3$CI). Once again the barriers to C−I cleavage, $\Delta E^{\ddagger}_{C-I}$, have been scaled using the field substituent constants of the reactants and are plotted in Figure 5. As in the case of the C−Cl cleavage reaction the substituents have no influence on the values of $\Delta E^{\ddagger}_{C-I}$ measured on the Pd(111) surface.[35] On the Ag(111) surface fluorination of the reactant does lower the $\Delta E^{\ddagger}_{C-I}$ but the reaction constant $\rho = -2.9 \pm 0.4$ is still very low when compared to that found for β-hydride elimination. Once again the results suggest that the transition state is reactant-like in the sense that there is little change in charge density distribution between the reactant and the transition state and thus little effect of fluorine substitution on the $\Delta E^{\ddagger}_{C-I}$.

To support the proposition being put forth, the literature has been surveyed to compile the reported values of the barriers to C−I and C−Cl cleavage on well-defined surfaces. If the transition state for these reactions is indeed reactant-like and occurs early in the reaction coordinate, these barriers ought to be relatively insensitive to the nature of the surface and the

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spread in their values ought to be relatively small. The values of $\Delta E^{\ddagger}_{C-I}$ and $\Delta E^{\ddagger}_{C-Cl}$ are reported in Figure 4 for methyl iodide, ethyl iodide and for alkyl chlorides on a large number of surfaces. These values range from 7 to 14 kcal/mol which, as the proposition suggests, is much narrower than the range observed for β-hydride elimination, the reaction with the late transition state.

Once again, some comment needs to be made concerning the sources of the barriers to dehalogenation included in Figure 4. The surfaces used have been those of metals, metallic alloys, and some modified metal surfaces. For the most part these have been single crystalline surfaces. In the case of C−I cleavage the kinetics have been studied most commonly using X-ray photoemission spectroscopy (XPS) to measure the coverages of reactants and products and to follow the extent of reaction during heating. In the case of C−Cl cleavage a number of methods have been used including thermal desorption methods and spectroscopic methods. As in the case of β-hydride elimination the majority of these studies do not attempt to measure the reaction barrier and the pre-exponent independently and often simply report a temperature range in which the reaction occurs during heating. To compare values on an equal footing it has been assumed for the purposes of this work that the preexponent is $\nu = 10^{13}$ s^{-1}. It is unlikely that the errors introduced by these assumptions are sufficient to change the basic result illustrated in Figure 4 which is that the barriers to dehalogenation are relatively insensitive to the nature of the surface.

One of the concerns that arises in looking at the type of data reported in Figure 4 is that while the barriers to β-hydride elimination have been measured on metal, semiconductor, and oxide surfaces, the barriers to dehalogenation have been measured primarily on metallic surfaces. Since the values of $\Delta E^{\ddagger}_{\beta-H}$ tend to be higher on the semiconductor and oxide surfaces than on the metals it might be the case that the values of $\Delta E^{\ddagger}_{C-I}$ and $\Delta E^{\ddagger}_{C-Cl}$ are also higher on the semiconductor and oxide surface and thus increase the range of the barriers to the dehalogenation reactions. Unfortunately, there do not appear to have been any careful studies of the kinetics of dehalogenation on the semiconductor surfaces. However, vibrational spectroscopy has shown that even adsorption at 100 K results in the dissociation of both CH$_3$Cl and CH$_3$I on the Si(100) surface.[36,37] This suggests that the $\Delta E^{\ddagger}_{C-I}$ and $\Delta E^{\ddagger}_{C-Cl}$ are quite low and in fact fall lower than the values on most metal surfaces shown in Figure 4. On many of those metal surfaces dissociation would not occur to a significant extent at temperatures as low as 100 K. Thus although the range of materials surfaces used for comparison of the barriers to β-hydride elimination and dehalogenation are not identical, there is no evidence that this issue undermines the general conclusion that the range of values of $\Delta E^{\ddagger}_{\beta-H}$ is in fact much greater than the range of values for $\Delta E^{\ddagger}_{C-I}$ and $\Delta E^{\ddagger}_{C-Cl}$.

6. Thoughts and Caveats

Section 1 of this paper presents the proposition that the $\Delta E^{\ddagger}$ to elementary surface reactions that have reactant-like transition states should be insensitive to the nature of the surface while the $\Delta E^{\ddagger}$ to reactions with product-like transition states should be sensitive to the nature of the substrate. This proposition is illustrated by the potential energy surfaces in Figure 1. Sections 2−5 have presented results that are supportive of the proposition but there are several underlying assumptions and caveats that should be kept in mind. When the transition state to a reaction is truly identical to either the reactant or the product, then the

proposition must hold true. If the transition state is identical to the reactant, the barrier, $\Delta E^{\ddagger} = 0$, will be independent of the surface. If the transition state is identical to the product, the barrier $\Delta E^{\ddagger} = \Delta E_r$ will depend on the nature of the surface. This has been illustrated in sections 2 and 3 using the simple cases of molecular adsorption and desorption.

For cases in which the transition state lies "between" the reactant and the product the applicability of the proposition becomes less rigorous. Its success must depend on the degree to which the transition state can be described as either reactant-like or product-like and this is not a rigorously definable quantity. Nonetheless, the proposition serves as a framework for thinking about the influences of surfaces on the $\Delta E^{\ddagger}$ to different types of reactions. The data chosen to support the proposition have been illustrated in Figure 4, and these data use the values of the barriers to the β-hydride elimination and dehalogenation reactions derived from the literature. It was then pointed out that the $\Delta E^{\ddagger}$ take on a wide range of values, $\Delta\Delta E^{\ddagger} \approx 32$ kcal/mol, in the case of β-hydride elimination for which there is evidence that the transition state is product-like. In the case of dehalogenation, for which there is evidence that the transition state is reactant-like, the range of values of $\Delta E^{\ddagger}$ is comparatively small, $\Delta\Delta E^{\ddagger} \approx 7$ kcal/mol. These examples suggest that the proposition holds for surface reactions with transition states that are reactant-like and product-like without being identical to either reactant or product. Furthermore, it is a testable proposition and can serve to guide the future investigations into effects of surfaces on the transition states to elementary surface reactions.

One of the underlying assumptions in the application of the proposition is that one knows that the transition state to a given elementary step on a surface can be described as either reactant-like or product-like. The proposition put forth in this article does not address this issue, only the consequences of the nature of the transition state. The classical approaches to thinking about the nature of the transition state would rely on relationships between kinetic barriers and reaction thermodynamics. The crudest would be Hammond's postulate which suggests that the transition states to exothermic elementary reaction steps are reactant-like while the transition states to endothermic steps are product-like.[38] The basis for this completely general postulate is questionable, and there are, of course, reactions for which one cannot realistically think of the transition state as falling into either class.[39] A somewhat more quantitative, although still empirical, approach is to define a transfer coefficient such as that of Evans and Polanyi. This uses measurements of $\Delta E^{\ddagger}$ and ΔE_r for a reaction with a set of related reactants (such as was done to examine substituent effects on dehalogenation and β-hydride elimination) to quantify the sensitivity of a reaction barrier to the reaction energy.

$$\alpha = \frac{d\Delta E^{\ddagger}}{d\Delta E_r}$$

Very low values of α indicate an early transition state while values of α approaching unity indicate a product-like transition state. The principle problem with the application of either of these methods to reactions on surfaces is the lack of measurements of reaction energetics ΔE_r for surface reactions. It remains the case that we tend to have much better measurements of reaction kinetics than we do reaction energetics or adsorbate−surface bond strengths (for most species). Instead it seems likely that ab initio molecular simulation will be the primary source of insight into the nature of the transition states for various elementary steps of surface reactions.

Limiting the classification of transition states to being either reactant-like or product-like is clearly a simplification which must be kept in mind when trying to apply the proposition to thinking about the effects of surfaces on the $\Delta E^{\ddagger}$ to elementary reaction steps. Ideally one would like to be able to define a scalar quantity that would determine the degree to which a transition state is either reactant-like or product-like. Such a scalar might correspond to the position of a transition state along some normalized reaction coordinate. The proposition should then be expected to hold for transition states within some limits of being reactant-like or product-like. Unfortunately, the classification of transition states for surface reactions along these lines is lacking and is probably something that can only be achieved by computational simulation.

It is important to point out the consequences of microscopic reversibility on the predictions of the proposition. All elementary reaction steps can be considered to have a microscopic reverse. In fact, the obvious example in this context is that molecular desorption is the reverse of molecular adsorption. Microscopic reversibility dictates that if the transition state is early in one direction then it is late in the reverse direction. This is illustrated quite clearly in Figure 1 if one considers the microscopic reverse to the top reaction with the product-like transition state. In the reverse reaction the product becomes the reactant and the reactant becomes the new product. As such, the transition state is now reactant-like and the $\Delta E^{\ddagger}$ to the reverse reaction will be insensitive to the nature of the surface where it was sensitive in the case of the forward reaction. Thus, what one knows about the effect of the surface on the $\Delta E^{\ddagger}$ to a given reaction has immediate implication for the effect of the surface on the $\Delta E^{\ddagger}$ to the reverse reaction.

Finally, it may also be the case that the corollary to the proposition is useful. Those elementary surface reactions which are found to have barriers that are sensitive to the nature of the surface may be predicted to have transition states that are product-like. Similarly those that have barriers that are insensitive to the nature of the surface may be predicted to have transition states that are reactant-like.

7. Catalytic Applications and Implications

If the proposition is taken to be valid, how would one apply it in a useful manner to the design of a new catalyst or the modification of an existing catalyst? Of course, real catalytic processes have very complex mechanisms but these do consist of elementary reaction steps. To begin thinking in a rational manner about the effects that changes to the catalyst surface might have on the reaction kinetics or selectivity one would need to know the reaction mechanism. At a minimum one would need to know something about the elementary steps which are either rate controlling or selectivity controlling. At this point if the elementary steps can be examined to determine whether their transition states are reactant-like or product-like one is in a position to apply the proposition. Of course, determining the nature of the transition state for the rate limiting step to a real catalytic process may not be a trivial undertaking. It requires resort to computational theory or to experiments which can truly isolate and probe the kinetics of that elementary step. In fact this should be one of the important roles of surface science and computational theory within the larger scope of catalytic science. Having characterized the nature of the transition state to the elementary steps that make up the reaction mechanism, modifications to a catalytic process can be aided by using the proposition to realize that changes will have the greatest effect on the $\Delta E^{\ddagger}$ and the kinetics of those reaction steps with late or product-like transitions states. As an example, the dehalogenation of alkyl halides to produce olefins has several steps: alkyl halide adsorption, carbon-halogen bond dissociation, β-hydride elimination in the alkyl group to produce the olefin, followed by olefin desorption and halide removal from the surface. Of these steps the first two have early transition states while β-hydride elimination and the desorption steps have late transition states. In the context of the proposition one would clearly expect that changes to the nature of the catalyst surface would have the greatest effect on the kinetics of the β-hydride elimination and desorption steps. Such changes to the nature of the surface would include changes in the substrate, changes in surface composition by addition of modifiers, or changes to the surface structure. Of course, the usefulness of the proposition would not include changes in the catalyst surface that result in a complete change in reaction mechanism or changes that are sufficiently extreme that they result in a change in the nature of the transition states for the elementary steps. In general, changes to the catalyst would be made to either increase or to decrease the $\Delta E^{\ddagger}$ to those steps with late transition states depending upon the desire net effect. By comparison, changes to the catalyst will be expected to have far less effect on the kinetics of the steps with the early or reactant-like transition states.

8. Conclusions

A proposition has been put forth which provides a framework for thinking about the effects of surfaces on the $\Delta E^{\ddagger}$ and the kinetics to elementary surface reactions in terms of the nature of their transition states. If the transition state is product-like then changes to the nature of the surface will have significant influence on the $\Delta E^{\ddagger}$. On the other hand, if the transition state is reactant-like, the $\Delta E^{\ddagger}$ will be relatively insensitive to changes in the catalytic surface. At this point this proposition is not quantitative but can be applied qualitatively. Furthermore, the proposition is testable given the current state of both experimental and computational methods for probing the nature of the transition states to elementary reactions occurring on surfaces. The hope is that these ideas will serve to stimulate further thought and guide further research in this area.

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