

Transition States for Surface-Catalyzed Chemistry

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ABSTRACT

Fluorine substituent effects have been used to probe the nature of the transition states for the several elementary reaction steps occurring on metal surfaces. The reactions described include β -hydrogen elimination in adsorbed alkoxide and alkyl groups, coupling of alkyl groups, and dehalogenation of alkyl chloride and iodides. The substituent effect method can provide a connection between heterogeneous catalysis, surface science, and computational molecular simulation of surface reactions.

Introduction

The transition state of an elementary chemical reaction has been the object of intense interest and investigation since classical transition state theory was first proposed in the mid-1930s.^{1,2} The zero-point energy difference between the reactant and the transition state is the activation barrier (ΔE_{act}) and dictates the reaction rate. As such, understanding the transition state lies at the heart of catalytic science. Catalysts increase reaction rates by opening reaction pathways with lower effective activation barriers than those in the gas phase. Consider the simple one-dimensional potential energy surfaces of Figure 1, which depict a prototypical reaction leading from reactant (R) to product (P) via both gas-phase and surface-catalyzed pathways. Each pathway passes through a transition state ($[\text{TS}]^\ddagger$). The goal of the research program described in this Account has been to probe the nature of the transition states for surface reactions with a view to providing the fundamental understanding that will ultimately lead to rational approaches to lowering the barriers to surface-catalyzed reactions.

Within the framework of transition state theory, the rate constant (k_{g}) for the elementary gas-phase reaction of Figure 1 is given by^{1–4}

$$k_{\text{g}} = \left(\frac{k_{\text{B}}T}{h} \right) \frac{q_{\ddagger}}{q_{\text{R}}} \exp\left(\frac{-\Delta E_{\text{act}}^{\text{g}}}{k_{\text{B}}T} \right)$$

The partition function for the reactant is given by q_{R} , while q_{\ddagger} is the partition function for all degrees of freedom in the transition state other than the reaction coordinate. The

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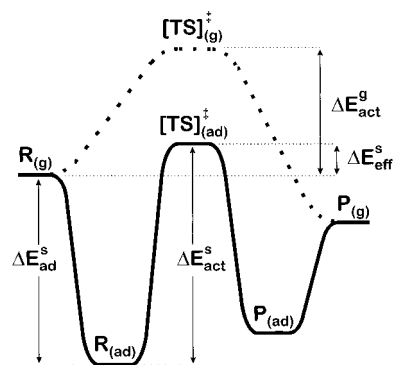


FIGURE 1. Schematic potential energy surfaces for the reaction $\text{R} \rightarrow \text{P}$. The dashed line represents the gas-phase pathway, which proceeds via a single elementary step through the gas-phase transition state $[\text{TS}]_{(\text{g})}^\ddagger$. The surface-catalyzed reaction proceeds via three elementary steps: (1) reactant ($\text{R}_{(\text{g})}$) adsorption, (2) conversion of $\text{R}_{(\text{ad})}$ to $\text{P}_{(\text{ad})}$ via an adsorbed transition state $[\text{TS}]_{(\text{ad})}^\ddagger$, and (3) product ($\text{P}_{(\text{ad})}$) desorption. As a result, the effective activation barrier to the surface-catalyzed process ($\Delta E_{\text{eff}}^{\text{s}}$) is lower than the activation energy to the gas-phase reaction, $\Delta E_{\text{act}}^{\text{g}}$.

surface-catalyzed reaction cannot be elementary since it must consist of a minimum of three sequential elementary steps: reactant adsorption, reaction, and product desorption. The adsorption step is characterized by an equilibrium constant (K_{ad}), while the reaction and desorption steps are characterized by elementary rate constants k_{r} and k_{d} , respectively. Under conditions in which $\text{R}_{(\text{g})}$ is equilibrated with a low coverage of $\text{R}_{(\text{ad})}$ and the product desorption is fast ($k_{\text{d}} \gg k_{\text{r}}$), the effective catalytic rate constant is

$$k_{\text{eff}} = K_{\text{ad}}k_{\text{r}}$$

The effective activation barrier is

$$\Delta E_{\text{eff}}^{\text{s}} = \Delta E_{\text{act}}^{\text{s}} - \Delta E_{\text{ad}}^{\text{s}}$$

and the catalyst has opened a reaction pathway with $\Delta E_{\text{eff}}^{\text{s}} < \Delta E_{\text{act}}^{\text{g}}$.⁵ The transition states and energy barriers to surface reactions pervade the framework used to think about catalytic phenomena. However, despite their importance, the transition states of surface-catalyzed reactions remain poorly described. Understanding of the nature of these transition states provides a key to unlocking a much deeper understanding of catalytic reaction kinetics.

This Account describes an approach to probing the transition states of surface-catalyzed reactions by using careful measurements of substituent effects on $\Delta E_{\text{act}}^{\text{s}}$. In a number of surface reactions, the reactants can be modified by substitution of fluorine for hydrogen atoms in a way that influences $\Delta E_{\text{act}}^{\text{s}}$ without changing the reaction mechanism. Surface science methods allow careful measurement of $\Delta E_{\text{act}}^{\text{s}}$ for elementary steps of such reactions. The effects of fluorine substitution then provide

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Table 1. Observations of Fluorine Substituent Effects on Metal Surfaces

reaction	chemical equation	surface	reaction constant (ρ), kcal/mol	refs
β -hydrogen elimination in alkoxides	$\text{RCH}_2\text{O}_{(\text{ad})} \rightarrow \text{RCH}=\text{O}_{(\text{ad})} + \text{H}_{(\text{ad})}$	Cu(111) Cu(100) Cu(110) Ag(110)	36	25, 26, 30 26, 54 26 26
β -hydrogen elimination in alkyls	$\text{RCH}_2\text{CH}_2_{(\text{ad})} \rightarrow \text{RCH}=\text{CH}_2_{(\text{ad})} + \text{H}_{(\text{ad})}$	Cu(111)		55
β -fluoride elimination in fluoroalkyls	$\text{RCF}_2\text{CH}_2_{(\text{ad})} \rightarrow \text{RCF}=\text{CH}_2_{(\text{ad})} + \text{F}_{(\text{ad})}$	Ag(111)		14
alkyl coupling	$2\text{RCH}_2_{(\text{ad})} \rightarrow \text{RCH}_2\text{—CH}_2\text{R}$	Ag(111)	18	30, 33
phenyl coupling	$2\text{RC}_6\text{H}_4_{(\text{ad})} \rightarrow \text{R}(\text{C}_6\text{H}_4)\text{—}(\text{C}_6\text{H}_4)\text{R}$	Cu(111)		42
dechlorination	$\text{RC—Cl}_{(\text{ad})} \rightarrow \text{RC}_{(\text{ad})} + \text{Cl}_{(\text{ad})}$	Pd(111)	-0.5	45, 46, 48
deiodination	$\text{RC—I}_{(\text{ad})} \rightarrow \text{RC}_{(\text{ad})} + \text{I}_{(\text{ad})}$	Pd(111) Ag(111)	-0.3 -2.9	48, 50 48, 49
deprotonation	$\text{RCO}_2\text{H}_{(\text{ad})} \rightarrow \text{RCO}_2_{(\text{ad})} + \text{H}_{(\text{ad})}$	Ag(110) Ag(111)		56, 57 57

a glimpse into the nature of the transition states for these elementary steps. The primary purpose of this Account is to give the reader a clear picture of the progress that has been made along this exciting new avenue into the understanding of reactions catalyzed by metal surfaces. A second purpose is to show that this approach forges links between experimental surface science, theoretical studies of surface transition states, and our understanding of heterogeneous catalysis.

Probing the Transition State

The study of transition states to surface reactions of catalytic interest is in its infancy.^{6,7} From both an experimental and a theoretical perspective, the environment of a metal surface is complex. Furthermore, many catalytically interesting reactions are complex multistep processes, and the total number of such surface reactions for which the mechanism is known is quite limited. However, the field of mechanistic catalytic surface chemistry is very active, and the number of well-defined surface reaction mechanisms is growing continuously. From a theoretical perspective, calculating potential energy surfaces for reactions on metals is complicated by the need to include large numbers of electrons. Again, rapid progress is being made in this field; however, the theoretical descriptions of transition-state structure and electronic structure contain a level of detail which cannot be verified experimentally.

The substituent method for probing the electronic characteristics of a surface transition state has been borrowed from physical organic chemistry.⁸⁻¹⁰ Imagine a reaction of the form



where Y is the portion of the molecule undergoing reaction, G is the molecular framework, which is fixed, and R is the substituent, which is varied systematically. The activation energy for the reaction will depend on the characteristics of the substituent ($\Delta E_{\text{act}}^{\text{R}}$) and can be compared to the activation energy for the same reaction with hydrogen as the substituent ($\Delta E_{\text{act}}^{\text{H}}$). The effects of the substituent can be quantified by

$$\Delta E_{\text{act}}^{\text{R}} - \Delta E_{\text{act}}^{\text{H}} = \rho\sigma^{\text{R}}$$

where σ^{R} is an empirically determined “substituent constant” that reflects the properties of the substituent and is independent of the nature of the reaction. The quantity ρ is particular to the reaction under study and quantifies the susceptibility of the reaction energetics to the properties of the substituents. Modern work in this area has divided the substituent properties into four types: field effects, electronegativity effects, resonance effects, and polarizability effects.⁸⁻¹⁰ As an example, in reactions with transition states that are electron deficient with respect to the initial state reactant,



ΔE_{act} is increased by substituents such as fluorine with high field effect substituent constants (σ_{F}). These energetically destabilize the cationic transition state with respect to the initial state. Thus, the response of ΔE_{act} to the substituents can be used as a means of probing the electronic nature of the transition state.

Application of Substituent Effects on Surfaces

Substituent effects have been applied successfully to the study of surface reactions through the use of fluorine as the substituent of choice. Table 1 gives a comprehensive list of the elementary surface reactions for which fluorine substituent effects have been observed. As the prototypical example, consider the β -hydrogen elimination reaction in alkoxides on a Cu(111) surface.

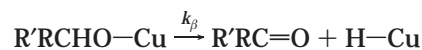


Figure 2 shows three temperature-programmed reaction spectra (TPRS) for β -hydrogen elimination in fluorine-substituted isopropanoxides. The TPRS show acetone desorption and are measures of surface reaction rate versus temperature. At this point, no interpretation is necessary beyond the observation that, as the degree of fluorination increases, the peak reaction temperature increases, implying that the $\Delta E_{\text{act}}^{\text{S}}$ increases.¹¹

Translating the successful application of substituent effects from homogeneous environments to the solid surface requires attention to several issues. First, the environment of the rigid solid surface is undoubtedly more sterically hindered than that of the solution or gas

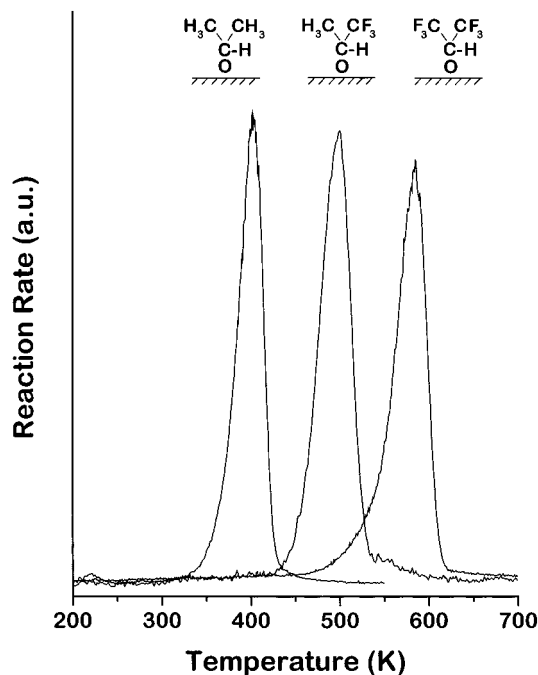


FIGURE 2. Thermally programmed reaction spectra of the decomposition of $(\text{CH}_3)_2\text{CHO}_{(\text{ad})}$, $(\text{CF}_3)(\text{CH}_3)\text{CHO}_{(\text{ad})}$, and $(\text{CF}_3)_2\text{CHO}_{(\text{ad})}$ on the Cu(111) surface. Decomposition by β -hydrogen elimination yields acetones, which then desorb rapidly from the surface. Fluorination of the methyl groups substantially lowers the rate of β -hydrogen elimination by raising the activation barrier $\Delta E_{\text{act}}^{\text{s}}$. This is manifested by the increase in acetone desorption temperature.

phase. In this sense, the choice of fluorine as a substituent is probably ideal in that it is relatively small and thus does not significantly perturb the size or geometry of the adsorbed reactant.^{12,13} Second, to interpret the effects of substituents in a rational manner, the mechanism of the reaction must be known, and fluorine substitution must not change the reaction mechanism. This is certainly a reaction-specific criterion, and examples can be cited in which fluorine substitution does, in fact, change reaction mechanisms.^{14–16} The successful studies reported in this Account were probably aided by the fact that the C–F bond is relatively strong (~ 110 – 125 kcal/mol).¹⁷ As a result, fluorine plays a passive role, influencing reaction kinetics without opening alternate reaction channels such as C–F bond cleavage. Finally, fluorine-containing substituent groups have a wide range of substituent constants and thus induce large variations in rate constants.^{9,10}

Methodology

This Account describes studies of the reaction kinetics of hydrocarbon and fluorocarbon reactants on single-crystal metal surfaces under ultra-high-vacuum conditions. The approach starts by identifying hydrocarbon surface reactions for which the mechanism is known. It is then necessary to determine that fluorination of the reactant does not change the reaction mechanism. This is accomplished by using spectroscopic measurements to identify the adsorbed intermediates and mass spectrometry to identify reaction products desorbing from the

surface. Having determined that the reaction under study meets these necessary conditions for the rational interpretation of substituent effects, we have measured reaction rates (r), rate constants (k), and activation energies ($\Delta E_{\text{act}}^{\text{s}}$) using a broad a range of fluorine substitution. The following sections describe three reactions for which it has been possible to probe the transition state using fluorine substituent effects.

β -Hydrogen Elimination

On many metal surfaces, alkyl groups and alkoxides with C–H bonds in the β -position with respect to the surface react by β -hydrogen elimination to yield olefins, aldehydes, or ketones.^{18,19}

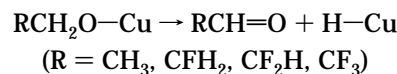


This is arguably one of the most important elementary steps in hydrocarbon surface chemistry. It is a key step in a number of partial oxidation processes, and its microscopic reverse is the olefin insertion reaction which initiates olefin hydrogenation.^{20–24}

The transition state for β -hydrogen elimination has been probed by selective substitution of fluorine into the terminal methyl groups of adsorbed alkoxides and alkyls. Alcohol and alkoxide surface chemistry has been studied extensively in investigations of partial oxidation catalysis by Ag and Cu surfaces.^{20,21} Figure 2 shows the reaction rate versus temperature during an experiment in which a Cu(111) surface is first prepared with isopropanoxides and then heated at a constant rate while acetone desorption into the gas phase is monitored. The desorption rate is a direct measure of the kinetics of β -hydrogen elimination. Fluorination of the methyl groups in isopropanoxides increases the product's peak desorption temperature by almost 200 K, revealing a substantial decrease in the reaction rate.

As a first step in the application of substituent effects to the study of any surface reaction, it is important to determine that fluorination of the reactant does not change the reaction mechanism. For all the alkoxides studied on the Cu(111) surface, the reaction products are the aldehydes or ketones expected from β -hydrogen elimination. Furthermore, the reaction rates measured using deuterated ethoxides ($\text{CH}_3\text{CD}_2\text{O}_{(\text{ad})}$ and $\text{CF}_3\text{CD}_2\text{O}_{(\text{ad})}$) exhibit strong kinetic isotope effects, consistent with β -hydrogen elimination being rate-limiting.²⁵ All evidence indicates that alkoxides on the Cu(111) surface react by β -hydrogen elimination, independent of their degree of fluorination.

Our current understanding of the transition state for β -hydrogen elimination comes from a study using fluorinated ethoxides on the Cu(111) surface.^{25,26}



The results are summarized by the potential energy profile

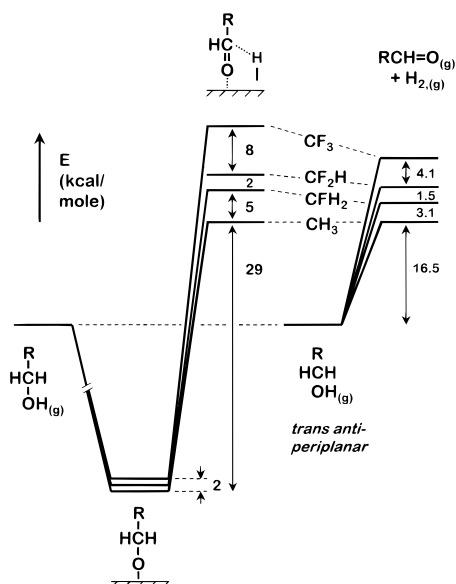


FIGURE 3. Potential energy diagram for the β -hydrogen elimination reaction in fluorinated ethoxides adsorbed on the Cu(111) surface. The reference energy level at the left is the energy of the gas-phase ethanol. Formation of the adsorbed ethoxides is only weakly influenced by fluorination. The activation barrier ($\Delta E_{\text{act}}^{\text{s}}$) to β -hydrogen elimination is increased dramatically by fluorination of the methyl group. At the right-hand side is the energy scale for the dehydrogenation of fluorinated ethanol 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 for dehydrogenation map directly onto the effects of fluorine on the activation barrier to β -hydrogen elimination. This suggests that the transition state is energetically late in the reaction coordinate.

of Figure 3. Starting with the gas-phase ethanol as the reference energy state, the heats of formation of the ethoxides are roughly independent of the degree of fluorination. The $\Delta E_{\text{act}}^{\text{s}}$ to β -hydrogen elimination, on the other hand, are highly perturbed by fluorination of the methyl group, increasing from 29 kcal/mol in $\text{CH}_3\text{-CH}_2\text{O}_{(\text{ad})}$ to 42 kcal/mol in $\text{CF}_3\text{CH}_2\text{O}_{(\text{ad})}$. Physically, the interpretation of this result is that the carbon atom at the reaction center is electron deficient in the transition state with respect to the initial state.



As a result, fluorination of the methyl group energetically destabilizes the transition state, thus increasing $\Delta E_{\text{act}}^{\text{s}}$. This interpretation is in agreement with computational investigations of β -hydrogen elimination and studies of this reaction in organometallic complexes.^{24,27,28}

A deeper insight into the nature of the transition state for β -hydrogen elimination comes from comparison of $\Delta E_{\text{act}}^{\text{s}}$ with the reaction energy for alcohol dehydrogenation in the gas-phase $\Delta E_{\text{r}}^{\text{g}}$.



The $\Delta E_{\text{r}}^{\text{g}}$ values have been determined computationally and are given at the right-hand side of Figure 3. Experiment has shown that fluorination of the methyl group increases the transition-state energy by 15 kcal/mol, while

computation has shown that fluorination increases $\Delta E_{\text{r}}^{\text{g}}$ for ethanol dehydrogenation by 9 kcal/mol.²⁵ Clearly, the bulk of the substituent effect on the $\Delta E_{\text{act}}^{\text{s}}$ can be attributed to its effect on $\Delta E_{\text{r}}^{\text{g}}$. A physically reasonable argument for this is that the loss of the H-CO bond and formation of a C=O bond leaves the carbon atom electron deficient with respect to the initial state. The direct implication is that the transition state looks much like the product and is "energetically" late along the reaction coordinate.

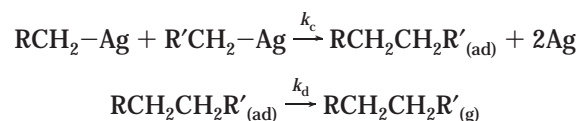
Fluorine substituent effects have also been observed in the β -hydrogen elimination of alkyl groups adsorbed on the Cu(111) surface. Our understanding of β -hydrogen elimination in adsorbed alkyls is very similar to that developed for alkoxides, although the investigation of β -hydrogen elimination in alkyls has not been as extensive.²⁹

One of the important points illustrated by the study of β -hydrogen elimination in the alkoxides is that the use of fluorine substituent effects offers a powerful avenue for comparison of experimental observations with computationally determined reaction energetics and barriers. In this sense, the method offers an approach to benchmarking the results of computational studies of transition states.

A second approach to quantifying the effects of substituents has been through the use of substituent constants such as those originally proposed by Hammett.⁸⁻¹⁰ Figure 4 illustrates the correlation between the field effect substituent constants (σ_{F})¹⁰ and the $\Delta E_{\text{act}}^{\text{s}}$ to β -hydrogen elimination in a large set of alkoxides. The slope or reaction constant is $\rho = 36$ kcal/mol and is typical in magnitude of a gas-phase reaction with an ionic transition state occurring late in the reaction coordinate. This is suggested by the schematic illustration in Figure 4 of a transition state looking much like the adsorbed product. This type of correlation allows prediction of $\Delta E_{\text{act}}^{\text{s}}$ and k_{r} for a wide range of substituted alkoxides. Equally importantly, these correlations can serve as the basis for comparison of the reaction on a Cu(111) surface with reactions such as alcohol dehydrogenation over high surface area catalysts.³⁰ This offers an important and useful avenue for connecting studies of reactions on single-crystal surfaces to reactions occurring on supported heterogeneous catalysts.

Alkyl Coupling

The second reaction of interest has been alkyl coupling on the Ag(111) surface. Adsorbed alkyl groups are generated by dissociative adsorption of the corresponding alkyl iodides.³¹ On the Ag(111) surface, adsorbed alkyl groups react by coupling to form alkanes, which desorb rapidly from the surface.^{31,32}



During heating, alkanes with twice the chain length of the

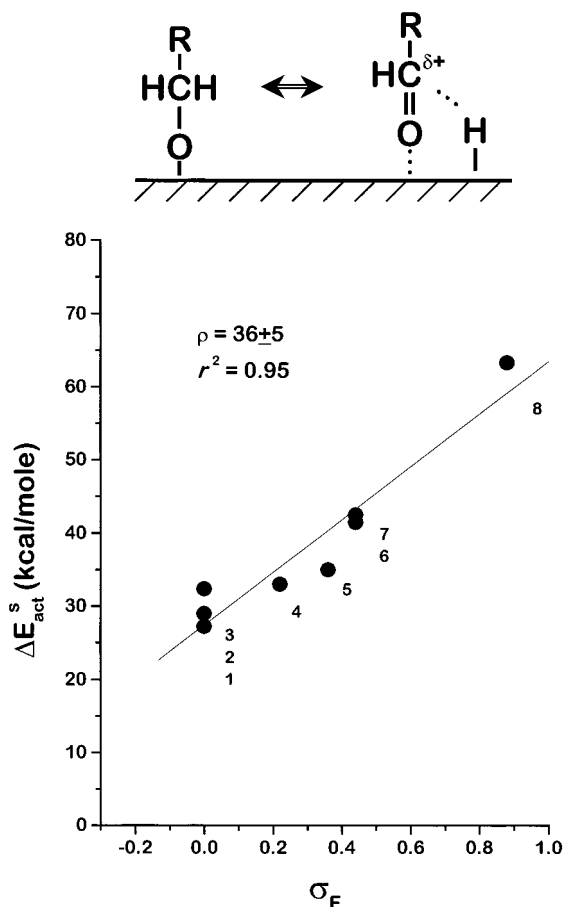


FIGURE 4. Activation energies for β -hydrogen elimination in alkoxides on Cu(111) plotted against the inductive substituent constants. These are defined as the sum of the inductive constants for the two substituent groups on the CHO reaction center. The activation barriers to β -hydrogen elimination increase with the degree of fluorination. 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 = $(\text{CH}_3)_2\text{CHO}_{(\text{ad})}$, 2 = $\text{CH}_3\text{CH}_2\text{O}_{(\text{ad})}$, 3 = $\text{CH}_3\text{O}_{(\text{ad})}$, 4 = $\text{CH}_2\text{FCH}_2\text{O}_{(\text{ad})}$, 5 = $\text{CHF}_2\text{CH}_2\text{O}_{(\text{ad})}$, 6 = $(\text{CF}_3)(\text{CH}_3)\text{CHO}_{(\text{ad})}$, 7 = $\text{CF}_3\text{CH}_2\text{O}_{(\text{ad})}$, 8 = $(\text{CF}_3)_2\text{CHO}_{(\text{ad})}$.

original alkyl groups desorb from the surface. Since $k_d \gg k_c$, measurement of the rate of alkane desorption serves as a measure of the kinetics of the alkyl coupling reaction.

In an effort to study the transition state for alkyl coupling, we have measured ΔE_{act}^s in a set of fluoroalkyl groups on the Ag(111) surface.³³ Figure 5 shows the measured ΔE_{act}^s versus the field substituent constants for the different substituents ($\sigma_F^R + \sigma_F^R$).¹⁰ As the degree of fluorination and the proximity of the fluorine atoms to the reaction center increase, $\Sigma\sigma_F^R$ increases. Clearly, ΔE_{act}^s increases substantially ($\rho = 18$ kcal/mol) with the increased level of fluorination.

The increase of ΔE_{act}^s for alkyl coupling with increasing fluorination suggests that the α -carbon atom in the transition state is electron deficient with respect to the initial-state alkyl group. The net effect is similar to the case of β -hydrogen elimination, in which the β -carbon atom at the reaction center becomes electron deficient in the transition state. Why should this be the case for alkyl coupling? Picture a transition state that is late in the

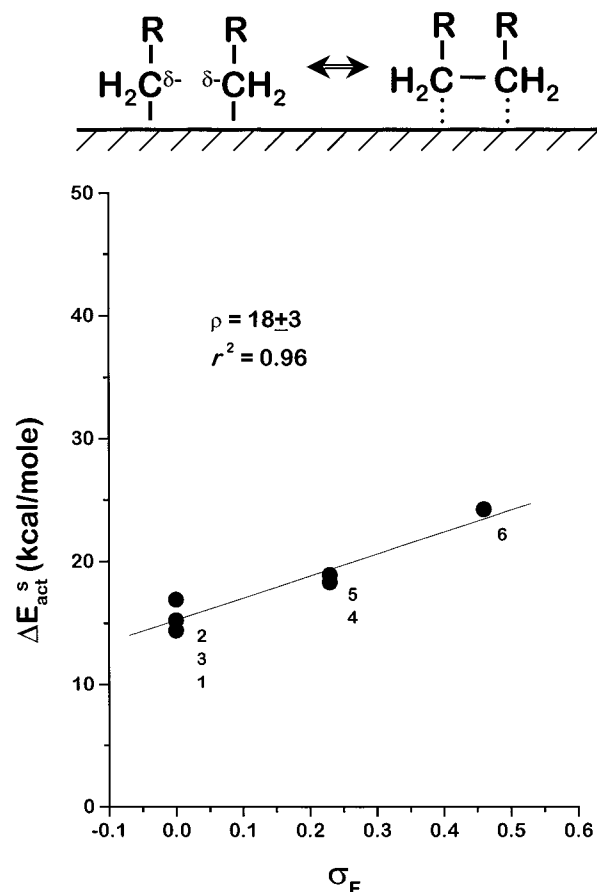
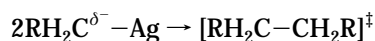


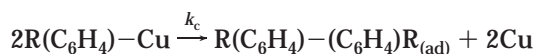
FIGURE 5. Activation energies for alkyl coupling on Ag(111) plotted against the inductive substituent constants. These are defined as the sum of the inductive constants for the substituents on the α -C of both alkyls. The activation barriers to alkyl coupling increase with the degree of fluorination and proximity of fluorine to the α -C at which coupling occurs. The implication is that the α -C in the transition state for alkyl coupling is electron deficient with respect to the initial state. 1 = $(\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)_2$, 2 = $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$, 3 = $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_3$, 4 = $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\text{CF}_3$, 5 = $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_2\text{CF}_3$, 6 = $\text{CF}_3\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\text{CF}_3$.

reaction coordinate and resembles the product alkane as depicted schematically in Figure 5. We could now ask whether the initial-state alkyl should be electron rich with respect to the transition state (or product).



Examination of the vibrational spectra of adsorbed alkyls suggests that this is the case. In CH_3CH_2- groups adsorbed on Cu, the ν_{CH_2} mode is softened and has a frequency of 2745 cm^{-1} .³⁴ Softening of the α -C-H stretching modes of alkyls has also been observed on Ni(111) and Pt(111) surfaces.^{35,36} One explanation is that charge is transferred from the metal surface into the σ_{CH}^* orbitals.³⁷⁻³⁹ While this may contribute to the net bonding of the alkyl groups to the surface, it weakens the α -CH bond. More importantly from the perspective of this work, it renders the α -CH₂ in adsorbed alkyl groups electron rich and thus may account for the apparent reduction in electron density in the transition state if it occurs late in the reaction coordinate, as depicted in Figure 5.

A test of the hypothesis described above for the alkyl coupling reaction has been performed by studying the phenyl coupling reaction on a Cu(111) surface.



Superficially, this reaction appears quite similar to the alkyl coupling reaction on the Ag(111) surface. However, the reactant phenyl groups have no α -CH bonds and cannot accept electron density in the same manner as alkyl groups. As a consequence, the phenyl coupling reaction should not and does not exhibit significant fluorine substituent effects.⁴⁰⁻⁴²

Dehalogenation

As the final example in this Account, the substituent effect methodology has been applied to the dehalogenation of alkyl halides, a reaction that is of both catalytic and environmental importance. Catalytic hydrodechlorination of chlorofluorocarbons (CFCs) is used to produce hydrofluorocarbons (HFCs), which are used as CFC alternatives in many applications.^{43,44} Hydrodechlorination is catalyzed by supported Pd particles in the presence of hydrogen.



One of the important steps in this process is the cleavage of C-Cl bonds, which falls into the general class of dehalogenation reactions. Dehalogenation has been investigated in a series of studies of the cleavage of both C-Cl bonds and C-I bonds on Pd(111) and Ag(111) surfaces.

The dechlorination reaction has been studied on the Pd(111) surface using a set of four substituted 1,1-dichloroethanes: CF_3CFCl_2 , CF_3CHCl_2 , CH_3CFCl_2 , and CH_3CHCl_2 . By measuring the adsorption energy ($\Delta E_{\text{ad}}^{\text{s}}$) and the effective barrier to dechlorination ($\Delta E_{\text{eff}}^{\text{s}}$), it has been possible to determine the intrinsic barrier to dechlorination ($\Delta E_{\text{C-Cl}}^{\text{s}}$).

$$\Delta E_{\text{C-Cl}}^{\text{s}} = \Delta E_{\text{ad}}^{\text{s}} + \Delta E_{\text{eff}}^{\text{s}}$$

All four values of $\Delta E_{\text{C-Cl}}^{\text{s}}$ are plotted in Figure 6 against the field substituent constants (σ_{F}).¹⁰ The important and most interesting observation is that the barrier to dechlorination is almost independent of fluorine substitution. This suggests that the transition state for cleavage of the C-Cl bond has an electron density distribution that is not much different from that in the reactant.^{45,46} In other words, the transition state for C-Cl cleavage occurs early in the reaction coordinate, as depicted in Figure 6.

The dechlorination reaction offers an excellent example of a reaction in which it has been possible to correlate the kinetics measured on single-crystal surfaces with kinetics observed on supported Pd catalysts at high pressures. Although the data in Figure 6 show that the $\Delta E_{\text{C-Cl}}^{\text{s}}$ is independent of fluorine substitution, the $\Delta E_{\text{eff}}^{\text{s}}$ increases as the amount of fluorine in the reactant increases. This is accompanied by a decrease in the overall

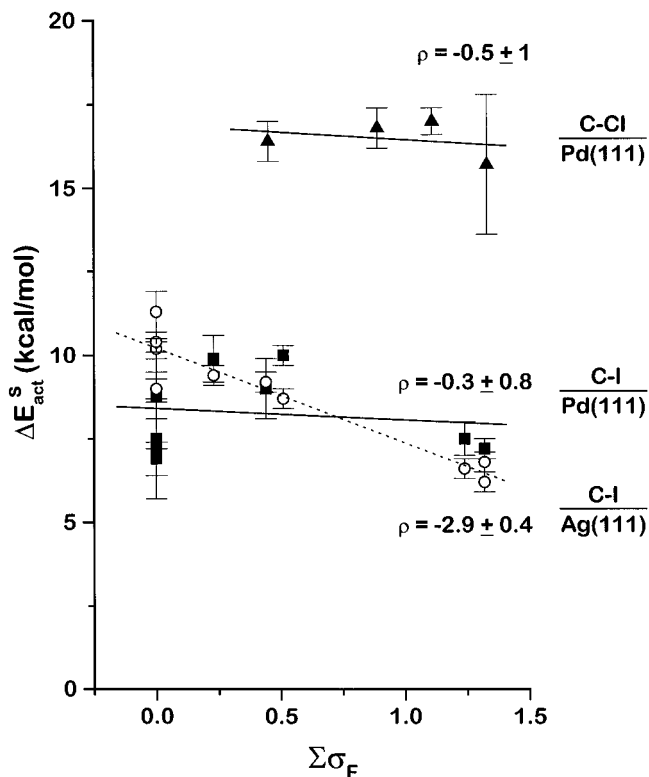
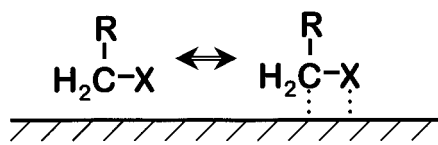


FIGURE 6. Activation energies for the dehalogenation of 1,1-dichloroethanes on Pd(111) and for alkyl and fluoroalkyl iodides on Ag(111) and Pd(111) surfaces plotted against the inductive substituent constants. In all cases the reaction constant, ρ , is very small, suggesting an early transition state which is similar to the reactant. The reactants used in the study of dechlorination were CF_3CFCl_2 , CF_3CHCl_2 , CH_3CFCl_2 , and CH_3CHCl_2 . The reactants used in the study of deiodination were R-I : $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, CH_2CF_3 , $\text{CH}_2\text{CH}_2\text{CF}_3$, $\text{CH}_2\text{CF}_2\text{CF}_3$, CF_3 , $\text{CF}_2\text{CF}_2\text{H}$, $\text{C}(\text{CF}_3)_3$.

rate of dechlorination and is due to the fact that the $\Delta E_{\text{ad}}^{\text{s}}$ decreases with increasing fluorination. Under high-pressure catalytic reaction conditions, it has also been observed that the rate constants for hydrodechlorination of dichloromethanes decrease with addition of fluorine.⁴⁷ This suggests that catalytic hydrodechlorination is rate limited by the dechlorination step and thus by the same transition state that has been examined on the Pd(111) surface. Such correlations between substituent effects for reactions on single-crystal surfaces and reactions on supported catalysts offer an important opportunity for deepening our understanding of catalysis by forging a stronger link with surface science.

The early transition state observed in our study of the dechlorination reaction has also been observed in studies of C-I cleavage on both Pd(111) and Ag(111) surfaces.⁴⁸⁻⁵⁰ This reaction has been studied using a very wide range of substituents on the C-I bond (R-I , $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$, CH_2CF_3 , $\text{CH}_2\text{CH}_2\text{CF}_3$, $\text{CH}_2\text{CF}_2\text{CF}_3$, CF_3 , $\text{CF}_2\text{CF}_2\text{H}$, $\text{C}(\text{CF}_3)_3$). Figure 6 also plots the values of

ΔE_{C-I}^S versus the field substituent parameters for cleavage of C–I bonds in this set of iodides. The interesting fact is that these studies reveal the same type of transition state as has been postulated for C–Cl cleavage. The reaction constants are negligible ($\rho = -2.9$ kcal/mol on Ag(111) and $\rho = -0.3$ kcal/mol on Pd(111)) when compared to those observed for reactions such as β -hydrogen elimination or alkyl coupling. When combined with the results for the dechlorination reaction, these results paint a consistent picture of dehalogenation reactions having early transition states on metal surfaces as depicted in Figure 6.

Opportunities

This Account has discussed several surface reactions for which it has been possible to use fluorine substituent effects to successfully probe the nature of transition states. A full list of the surface reactions for which fluorine substituent effects have been observed is given in Table 1. This approach provides an unprecedented look at the real nature of “reactivity” on surfaces and offers a wealth of opportunities to expand the scope of our understanding of surface chemistry. One of the attractions to this approach is that it is widely applicable, since it merely involves the careful extension of experiments that are commonly used to study hydrocarbon surface chemistry. These experiments also offer an opportunity to make connections between single-crystal surface chemistry and high-pressure catalytic chemistry on supported metals. Along another avenue, one can see an opportunity to make connections to computational descriptions of surface-catalyzed reactions.

Using substituent effects to make the link between single-crystal surface chemistry and heterogeneous catalysis requires some thought and care. In principle, there is no reason why measurements of reaction rates and rate constants over heterogeneous catalysts cannot be made using a set of fluorinated reactants, as has been done on single-crystal surfaces. Substituent parameters could then be used to correlate reaction rate constants or ΔE_{eff}^S among different reactants. One such connection has been pointed out in the example of the dechlorination of CFCs by Pd surfaces and supported Pd catalysts.^{47,48} Other examples can be found in the catalysis literature.^{51,52} One very interesting case is a study of alcohol dehydrogenation over CrO–ZnO catalysts.⁵³ This reaction is believed to occur via a mechanism which involves formation of an alkoxide followed by β -hydrogen elimination to yield aldehydes or ketones. It has been studied at atmospheric pressures using a number of substituted alcohols.⁵³ Plotting the data from that work using the same inductive substituent parameters used for β -hydrogen elimination, we find a reaction constant of $\rho = -6$ based on the use of a dimensionless ratio of rate constants rather than ΔE_{act} . For comparison, the reaction constant for β -hydrogen elimination in alkoxides on the Cu(111) surface yielded $\rho = -26$ (when obtained using the rate constant (k) rather than ΔE_{act}^S).³⁰ The fact that the reaction constants on

both surfaces are negative suggests that they reveal the characteristics of a transition state that is similar in nature and rate controlling for both processes.

The experimental quantities reported in this Account also have the potential to serve as benchmarks for computational efforts to calculate ΔE_{act}^S and transition-state structures for surface reactions. These computational efforts are receiving a great deal of attention and are an area of rapid progress and enormous opportunity.^{6,7} The link between computationally determined reaction energetics and experimentally determined activation energies has already provided valuable insight into the nature of the transition state for β -hydrogen elimination. In computational studies of transition states for hydrocarbon surface reactions, it would be conceptually straightforward and instructive to perform parallel calculations including fluorine as a substituent. The predictions of these calculations ought to be directly comparable to the effects of fluorine substitution on ΔE_{act}^S measured and reported in this Account. Furthermore, such calculations would reveal directly the nature of charge distributions in transition states. In principle, these approaches provide a direct link from theory to surface science to catalysis that offers an exciting opportunity to deepen substantially our understanding of surface reactivity.

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