



The transition state in catalytic surface chemistry

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Abstract

The transition states for the elementary steps of a catalytic surface reaction mechanism determine the overall rates of catalytic processes. Unfortunately, our understanding of the nature of transition states on surfaces remains very poor due to the extreme difficulties associated with experimental and computational methods for probing such metastable species. Currently progress is being made along three fronts: state-resolved molecular adsorption and desorption experiments, measurements of substituent effects on reaction barriers, and the use of computational simulation. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Catalytic kinetics and surface transition states

Chemical reaction kinetics lie at the core of catalytic phenomena. In order to understand catalytic processes we think in terms of complex multistep chemical reaction mechanisms which must include at least: reactant adsorption, conversions of stable surface species, and ultimately the desorption of products from the catalyst surface [1,2], as illustrated in Fig. 1. A great deal of effort over the past century has been focused on the elucidation of catalytic reaction mechanisms. However, mechanism addresses only half of the problem of trying to understand kinetics. The reaction mechanism is a set of elementary steps with associated rate constants (k) that ultimately dictate the overall reaction rate and selectivity. For a given elementary step the dominant term in the rate constant is the activation barrier (ΔE^\ddagger). This is the difference in zero-point energy between the stable reacting species and the transition state, the species at the maximum along the minimum energy pathway leading to the next stable intermediate in the mechanism. While there has been a great deal of success in the past at characterizing the nature of the stable intermediates of catalytic reaction mechanisms, comparatively little effort has gone into the characterization of transition states [3,4].

Experimental probes of the transition state are not trivial in the gas phase and are even more difficult on a catalyst surface. This is due in part to the fact that one has to isolate a truly elementary process leading from one stable

intermediate to another via a single well-defined transition state. In addition, the transition state itself is metastable and only exists for periods on the order of femtoseconds. Progress in the study of gas phase chemical reactions has reached the point that the Nobel prize in chemistry for the year 2000 was awarded to A. Zewail for the development and application of femtosecond spectroscopic methods. Similar experiments on surfaces and on catalysts lag far behind those in the gas phase [**5,6].

The 1999 Nobel prize in chemistry was awarded to J.

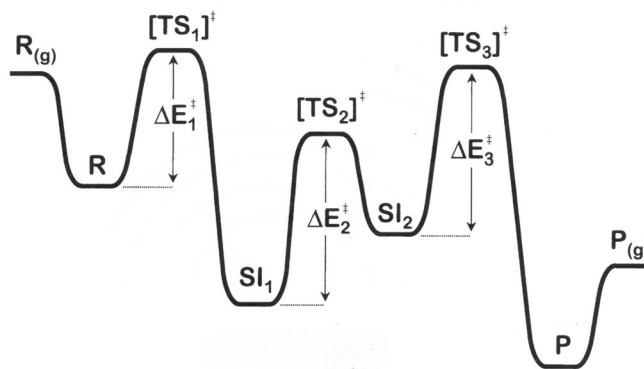


Fig. 1. A schematic of the one-dimensional potential energy surface for a hypothetical surface reaction mechanism in which a gas phase reactant, R, adsorbs on a surface and reacts via several stable intermediates, SI_n , to form a product, P, that desorbs into the gas phase. Each of the stable surface species including the adsorbed reactant and product are separated by reaction barriers at the top of which sit the transition states, $[TS_n]^\ddagger$, for each of these elementary steps. This schematic grossly simplifies the process by considering only a one-dimensional path through what is in reality a very complex multi-dimensional potential energy surface. Furthermore, it only attempts to depict the energy surface for a purely sequential process without parallel processes or branches.

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Pople and W. Kohn for their work leading to the evolution of computational methods into a core discipline within chemistry. Computational descriptions of the transition states are at the leading edge of work in the field of computational quantum chemistry. The difficulties associated with the computational characterization of transition states for surface reactions arise from the fact that one has to model quite large systems of atoms often involving many degrees of freedom and many electrons. While these issues plague the modeling of stable catalytic species they are compounded in the identification of transition states by the fact that one is searching for a saddle-point on a potential energy surface. Algorithms for such searches are much less well-developed than those for finding stable species at energy minima [7–9].

Just what is it that we would like to know about the nature of the transition state? In principle, the same properties as for stable intermediates: energy, atomic structure, electronic structure, vibrational modes, etc. These give the position of the saddle point in the potential energy surface between reactant and product, its energy, and its local shape. When combined with the same information about the reactant this would be sufficient to determine a rate constant at the level of a transition state theory description.

This article attempts to put into perspective the recent

developments in three probes of the transition states for surface reactions: state resolved adsorption/desorption studies, the measurement of substituent effects on reaction barriers, and the use of computational theory. Each provides different types of information with different levels of detail and reliability and different limitations of scope and application. Together, however, they offer an opportunity for real progress in our future understanding of the transition states to surface catalyzed reactions.

2. State resolved adsorption and desorption

The most detailed experimental probes of the transition states for surface reactions are those of direct dissociative adsorption or associative desorption processes such as H_2 or N_2 on $\text{Cu}(111)$. These occur without the intermediate formation of trapped molecular species in thermal equilibrium with the surface. Studies of these types of processes can be performed by measuring the reactive sticking probability of molecules in well-defined quantum states. This requires preparation of impinging molecules with controlled translational, electronic, vibrational, and rotational states as illustrated in Fig. 2A [10].

An experiment which is directly related and complementary to state resolved adsorption is measurement of the

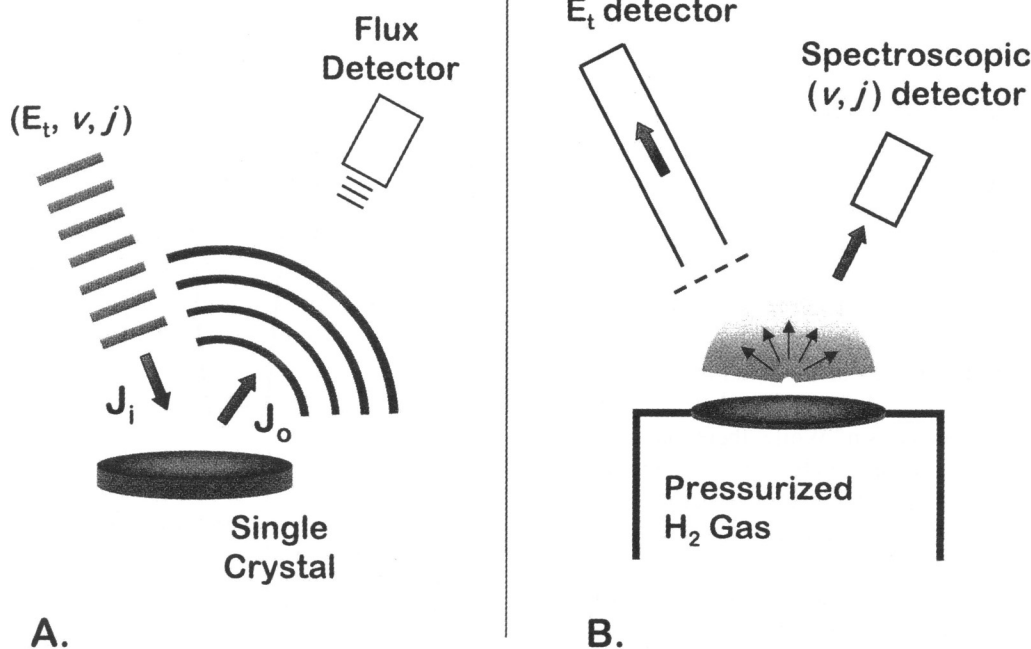


Fig. 2. Schematic illustrations of the state resolved adsorption and desorption experiments. These experiments exist in a variety of implementations. A. The adsorption experiment in which pulses of molecules are incident on the surface with well-defined translational (E_t), vibrational (ν) and rotational (j) states. The difference in the incident flux (J_i) and the scattered flux (J_o) is a measure of the sticking probability. B. The desorption experiment in which H atoms diffusing through a very thin crystal at high temperature desorb from the surface into vacuum. There the translational and/or internal state distributions are determined using time-of-flight and spectroscopic methods.

state distribution of desorbing molecules. For example, Fig. 2B illustrates an experiment in which H atoms diffuse through a thin single crystalline membrane and then desorb into the gas phase where their translational, vibrational, and rotational energy distributions are measured by time-of-flight and spectroscopic methods. The state resolved adsorption and desorption measurements are exactly related by microscopic reversibility. A very clear account of the conditions under which this is truly observed and the relative merits of the two experiments has been published recently by A. Hodgson [**11].

Direct adsorption or desorption occurs when the adsorbing or desorbing molecule does not encounter a potential energy well on approaching or leaving the transition state for either dissociative adsorption or associative desorption. As a result, the initial quantum state of the adsorbing molecules influences the sticking probability. Similarly the final state distribution of the desorbing molecules directly reflects the shape of the potential energy surface and serves to probe the nature of the transition state. As an example consider the schematic potential energy surface of Fig. 3 for the direct desorption of a diatomic from a surface. This plots only the portion of the potential energy surface describing the atom–atom separation (d) and the distance from the surface (z), averaging over all other degrees of freedom. The transition state occurs early in the desorption path with a very large value of d compared to that of the gas phase molecule (d_0). Such a transition state would manifest itself in desorption as vibrationally excited prod-

uct. This has been observed extensively for H_2 on Cu(111) and other metal surfaces [11]. Microscopic reversibility dictates that this would be reflected in higher sticking coefficients for vibrationally excited incident molecules. The potential energy surface has been computed recently for N_2 on Cu(111) [12] and experimentally it has been shown that at a surface temperature of 700 K desorbing N_2 has a vibrational temperature of 5100 K. Both clearly suggest a transition state of the type depicted in Fig. 3 [13].

Eigenstate resolved molecular beams also reveal properties of the transition state for direct adsorption. A recent set of experiments on the (2×1) reconstruction of the Pt(110) surface has studied the dissociative adsorption of CH_4 with controlled translational and the vibrational energy distributions [**14,15]. The dissociation is clearly assisted by vibrational excitation suggesting that the transition state requires an extended C–H bond. In addition it is suggested that the low translational energy sticking is influenced by a steering mechanism which favors molecules in low rotational states. This is a very interesting observation although similar observations on Ir surfaces have been interpreted in terms of CH_4 trapping in a shallow adsorption well [16–18]. This issue will undoubtedly receive further study before it is completely resolved.

3. Substituent effect probes of transition states

Substituent effects modify the barriers to surface reactions and can be used to probe surface processes without a gas phase product or reactant as in the experiments just described. However, substituent effects are limited to use with organic species that can be modified by the addition of substituent groups. The idea originates from the field of physical organic chemistry and is illustrated in Fig. 4. One first prepares a surface with adsorbates such as alkyl groups having a variety of different substituents such as partially fluorinated methyl groups. In this case the substituents influence the activation barrier for alkyl decomposition by β -hydrogen elimination. If the reaction center in the transition state is cationic with respect to the reactant alkyl group, then fluorination of the substituent will increase the barrier. Experimentally, one simply measures the kinetics of surface reactions in sets of substituted reactants. In the case of propyl groups (RCH_2CH_2-) and ethoxy groups (RCH_2O-) that react by β -hydrogen elimination it has been observed that the barrier is increased by fluorination of the substituent methyl group, implying that the reaction center in the transition state is cationic with respect to the reactant [19,20].

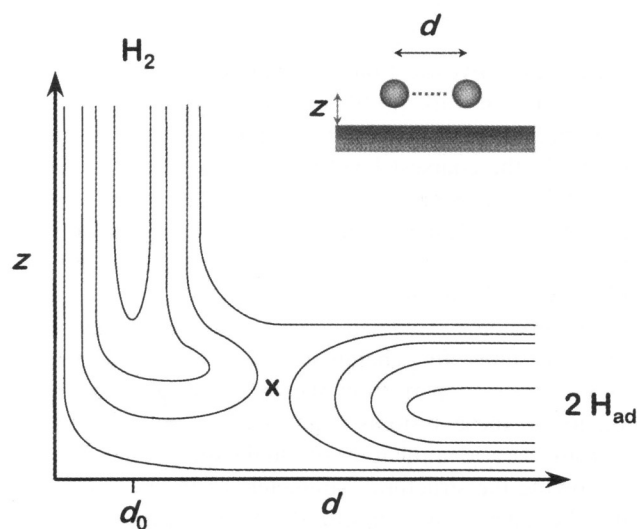


Fig. 3. A schematic two-dimensional potential energy surface for the dissociative adsorption or associative desorption of H_2 from the Cu(111) surface. The function is plotted as contours in energy versus the H–H bond length, d , and the height of the H_2 molecule above the surface, z . The energy averages over all other degrees of freedom. The gas phase H_2 bond length is d_0 . The transition state is marked with an X and occurs with the molecule close to the surface and with an extended H–H bond. As a result during desorption there is energy released into vibration. Similarly, excitation of vibration in the incident molecule enhances the dissociative sticking probability.

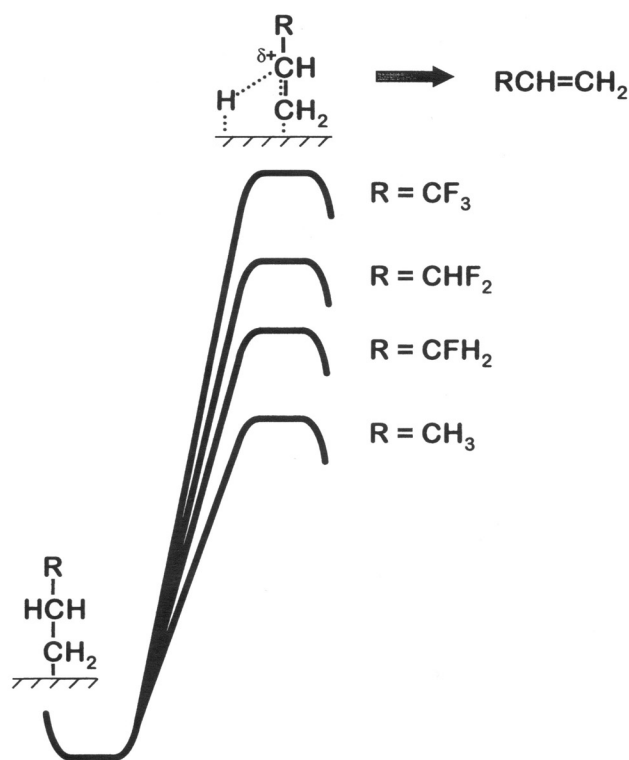


Fig. 4. The effect of substituents on the barrier to β -hydrogen elimination in fluorinated propyl groups to form propylenes. In the case of a transition state which has a reaction center (β -carbon atom) which is cationic with respect to the initial state, the effect of fluorine is to increase the reaction barrier. This is due to the increasingly destabilizing interaction between the methyl group and the carbon atom in the transition state as the degree of fluorine substitution is increased.

The scope of the use of substituent effects to probe surface reactions has been reviewed quite recently [21]. That review also describes the criteria for a reaction to be suitable for substituent effect studies of the transition state. Several studies have involved reactions of organic surface species that have been modified by various alkyl and fluoroalkyl groups. The successful use of fluorine substitution is due to the fact that the C–F bonds are unreactive but have large field effects that influence the barriers to reactions involving charge redistribution between reactant and transition state [22].

One of the attractive features of the use of substituent effects is that they can be quantified using tabulated substituent constants [22,23]. This allows comparison of substituent effects for a given reaction between surfaces. There have been attempts in the past to describe catalytic reactivity of different molecules using these empirical substituent constants [24,25]. What is potentially most important is that substituent effects can, in principle, serve as a means for comparison of reactions on well defined single crystal surfaces with the more complex environments of heterogeneous catalysts [26]. This could serve as a direct link between the fields of surface science and catalysis.

Another potentially important role for substituent effects is as benchmarks for computational studies of transition states. The experimentally determined effects of substituents on the barriers to surface reactions can be compared directly to the same effects determined computationally. Such comparisons would serve as tests of computational methods and link theory with experiment. Although this has not been attempted yet, a recent paper takes the first step in this direction by comparing the barriers measured for the β -hydrogen elimination of fluorine substituted ethoxy groups on Cu(111) with computationally determined reaction energies (ΔE_r) for the dehydrogenation of fluorine substituted ethanol to acetaldehydes [19,27].



This shows a direct correlation between the barriers to β -hydrogen elimination and the energetics of ethanol dehydrogenation which implies that β -hydrogen elimination has a late transition state that looks like the product acetaldehyde, as depicted in Fig. 4.

4. Computational models of transition states

The search for transition states is one of the most challenging problems in computational quantum chemistry. This is particularly true for attempts to model catalytic processes which necessarily requires predictions of reaction kinetics [7–9]. At the core of computational studies is the chosen method and the choice of the model for the system under investigation. The bulk of the computational work done on this problem has made use of density functional theory (DFT) to determine the electronic energy. At the coarsest level the models used for surfaces and catalysts can be broken into two categories: clusters and slabs. The cluster models use finite numbers of atoms while slab models are built into infinite arrays of unit cells with periodic boundary conditions.

The problems associated with the identification of transition states for chemical reactions on surfaces or catalysts arise in part from the fact that adequate representation of these systems requires many atoms and many electrons. The identification of stable species can be done by allowing the structural parameters of the model to vary until the energy is minimized. A transition state is a maximum in energy along one degree of freedom but a minimum with respect to all others. The algorithms for finding such saddle points in the potential energy function are not as well developed as those for finding minima.

The beauty of computational methods is, of course, that they provide a complete description of the system being investigated at a level of detail that is far beyond anything that will ever be achieved experimentally. In the case of a transition state this includes: energy, atomic structure,

electronic structure, vibrational frequencies, etc. In other words, all the characteristics that one ideally hopes to understand. It is important to remember that many of the quantities that can be derived from a computational study of a transition state cannot be checked experimentally. Although the computed barrier to a reaction might be compared to experiment, many other properties cannot. Andzelm et al. give a very comprehensive account of the reliability of computed properties of surface reactions [28]. Among other things they note that an extensive comparison of experimental and computed values for systems involving only first and second row atoms yields average errors of greater than 20 kJ/mole for density functional methods. From the point of view of reaction kinetics of course this can lead to errors of orders of magnitude. It is interesting to note that although DFT methods may not necessarily give good values for energetics, even for stable species, the accuracy of structural parameters can be quite good.

There are a number of recent applications of DFT methods to the study of transition states on surfaces. There have been three studies of CH_3 dehydrogenation to $\text{CH}_2 + \text{H}$ on the Ni(111) using density functional theory that serve as an interesting case for comparison [29,30,31]. The two most recent give values of 68 and 102 kJ/mole for the barriers. The structures for the transition states, however, are not so different and suggest that the reaction occurs by cleavage of a C–H bond over the top of a Ni atom. The C–H bond lengths in the transition states are 1.80 and 1.77 Å with Ni–H distances of 1.55 and 1.50 Å. Another very recent study of the same reaction on the Ru(0001) surface reveals a similar transition state structure with the C–H bond breaking over the top of a Ru atom [32]. Other examples of the application of DFT to reactions on metal surfaces include the calculation of potential energy surfaces for H_2 and N_2 dissociation on Cu(111) and Cu(100) surfaces used to interpret the results of molecular beam adsorption experiments [12,13,33].

5. Conclusions

Probing and understanding the transition states for surface catalyzed reactions is one of the great challenges in the field of catalytic surface chemistry. The means for doing this are at hand but not fully developed and certainly far from broadly applied. The problem is certainly one that is ripe for close collaboration between computational theory and experiment since it seems quite clear that the level of detail that can be expected from experiment is limited. Ultimately, computation may be the only approach to obtaining the level of detail that is desired, however, it there is a great need for overlap between the systems studied experimentally and computationally in order that there be adequate benchmarking of the results of computational methodologies. Such comparisons can be made with

either the results of state specific adsorption/desorption experiments or with observed substituent effects on reaction barriers. These are the types of experimental kinetic data that are available for truly elementary reaction steps.

What would we do with an understanding of the nature transition states to surface reactions, if it was in hand? Certainly combining such understanding with a mechanism would allow a complete description and modeling of the kinetics of complex reaction networks. More importantly, however, it opens the door to the solution of the next really important problem: how do the characteristics and the properties of a surface influence the barriers to catalytic reaction steps? Without understanding the nature of both stable intermediates and transition states on surfaces this question cannot be answered at the most fundamental level.

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