

Using β -hydride elimination to test propositions for characterizing surface catalyzed reactions

Xin Li ^a, Andrew J. Gellman ^b, David S. Sholl ^{b,*}

^a Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

^b Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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Abstract

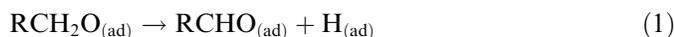
We describe the transition states determined using plane wave Density Functional Theory (DFT) for the β -hydride elimination reaction $\text{RCH}_2\text{O}_{(\text{ad})} \rightarrow \text{RCHO}_{(\text{ad})} + \text{H}_{(\text{ad})}$ on Cu(111) for $\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{F}, \text{CHF}_2,$ and CF_3 . Our results allow us to assess qualitative descriptions of these transition states based on previous experiments. Our calculations confirm that the character of the transition state is unaffected by fluorine substituents and the transition state for the forward reaction is late. By considering β -hydride elimination from adsorbed methoxy on multiple metal surfaces using DFT, we have examined the hypothesis that surface catalyzed reactions with product-like transition states are more structure sensitive than reactions with reactant-like transition states.

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1. Introduction

Transition states define the reaction rates of surface catalyzed reactions, but direct experimental characterization of surface transition states is challenging. Here, we describe the transition states determined using plane wave Density Functional Theory (DFT) for the β -hydride elimination reaction



on Cu(111) for $\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{F}, \text{CHF}_2,$ and CF_3 . Our results allow us to assess qualitative descriptions of these transition states based on previous experiments [1,2]. These experimental descriptions rely on making a connection between substituent effects on reaction activation energies, ΔE_{act} , and characterization of transition states as reactant-like or product-like. More importantly, our results allow us to test the recently advanced proposition that

surface reactions with product-like (reactant-like) transition states are relatively sensitive (insensitive) to the nature of the catalyst surface [3–5].

2. Calculation methods

We determined the activation energies for Eq. (1) using plane wave Density Functional Theory (DFT) with PW91-GGA as implemented in VASP [6–9]. We have shown previously that the adsorbate geometries of fluorinated ethoxy species on Cu(111) predicted using DFT are in excellent agreement with geometries predicted from IR adsorption data [10–13]. Our calculations used a $5 \times 5 \times 1$ k -point grid and a cutoff energy of 29.2 Ry in studying ethoxy, while a cutoff of 31.3 Ry was used to examine fluorinated species. Our previous calculations [10] showed that surface relaxation plays at most a minor role in the adsorption of $\text{RCH}_2\text{O}_{(\text{ad})}$, so our calculations were performed with a 5 layer slab with the metal atoms fixed. All calculations used a (3×3) surface unit cell containing a single adsorbed molecule. A vacuum spacing of 14 Å was used in all calculations. Transition states were located using the Nudged

* Corresponding author. Tel.: +1 412 268 4207; fax: +1 412 268 7139.
E-mail address: sholl@andrew.cmu.edu (D.S. Sholl).

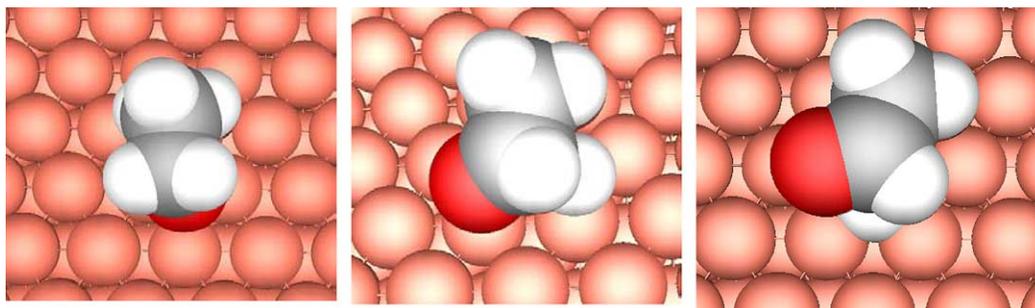


Fig. 1. Top views of the initial state (left), transition state (middle), and final state (right) for β -hydride elimination of ethoxy on Cu(111). The surface H atom is below the molecule in the final state.

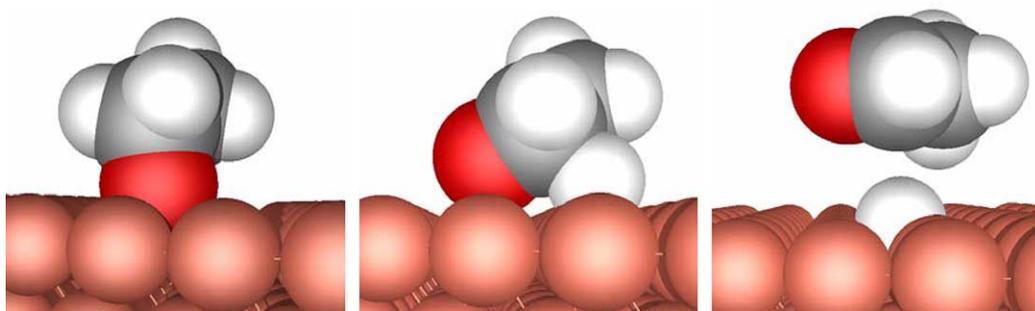


Fig. 2. Side views of the three adsorption configurations shown in Fig. 1.

Elastic Band (NEB) method allowing all adsorbate degrees of freedom to relax [14]. Multiple refinements of the minimum energy path connecting the reactants to products were typically necessary to localize the final transition state. The highest energy image from each final NEB calculation was optimized using an algorithm that converges to a critical point of the potential energy surface. Figs. 1 and 2 show the configurations determined using DFT for $R = CH_3$ in Eq. (1).

3. Results and discussion

The activation energies calculated using DFT for the reaction above and the reverse reaction are listed in Table 1. These activation energies are also plotted in Fig. 3 as a function of the substituent constants of the R group of

Table 1

Activation energies and geometry changes for selected coordinates for the forward (\rightarrow) and reverse (\leftarrow) reactions, with energies in kcal/mol, lengths in Å, and angles in degrees

	R = CH ₃	R = CH ₂ F	R = CHF ₂	R = CF ₃	R = H
$\Delta E_{act}^{\rightarrow}$	29.7 (29.1)	34.1 (33.0)	36.4 (35.1)	40.4 (42.2)	30.9 (32.5)
$\Delta E_{act}^{\leftarrow}$	13.8	15.0	13.1	15.0	8.3
$\Delta d_{C-H}^{\rightarrow}$	0.70	0.68	0.69	0.56	0.58
$\Delta d_{C-O}^{\rightarrow}$	-0.17	-0.17	-0.16	-0.15	-0.13
$\Delta d_{C-O}^{\leftarrow}$	0.05	0.05	0.05	0.05	0.08
$\Delta \theta_{O-C-C}^{\rightarrow}$	10.0	6.7	8.7	5.6	-
$\Delta \theta_{O-C-C}^{\leftarrow}$	-2.5	-3.8	-2.0	-2.8	-

All quantities are defined by the value at the TS minus the value for the reactant. Experimental data [1,2] are shown in parentheses.

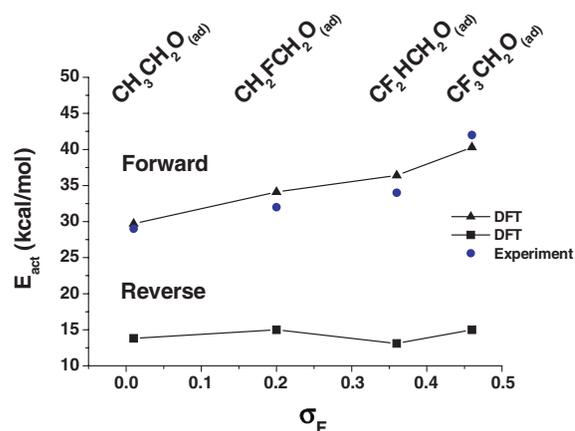


Fig. 3. DFT (■ and ▲) and experimental results [1,2] (●) for the activation energy of forward and reverse β -hydride elimination on Cu(111) plotted as a function of the field substituent constants, σ_F , of the substituted methyl groups.

the reactant [1]. Several points can be observed from these results. The agreement between the DFT and experimental results for the forward reaction is excellent. The barriers to the reverse reaction cannot be determined experimentally. The forward reaction shows a strong substituent effect [3]; as the degree of fluorination of the substituent group is increased the reaction activation energy increases. By contrast, E_{act} for the reverse reaction is essentially independent of the substituent.

Experimental characterization of transition states via-substituent effects relies on the assumption that the substit-

uents do not change the characteristics of the transition state of interest. Our DFT calculations demonstrate that this assumption is accurate for Eq. (1) on Cu(111). For example, the C–O bond length in the transition states with $R = \text{CH}_3$, CH_2F , CHF_2 , and CF_3 are all 1.26–1.27 Å. The O–C–C bond angles in the same transition states lie in the range of 119°–121°, compared to 111°–113° in $\text{RCH}_2\text{O}_{(\text{ad})}$. Other measures of the internal geometry of the adsorbed molecule in the transition state show a similar level of consistency as the substituent is varied.

Previous analysis of the experimental data shown in Table 1 [1,2], argued that the strong substituent effect in the forward reaction is consistent with the transition state being product-like. The reverse reaction must then have a reactant-like transition state and by the same reasoning should exhibit a weak substituent effect. Our DFT results allow us to examine this reasoning by characterizing the geometry of each transition state. Table 1 lists several bond length and bond angle differences between the reactant and transition state in both the forward and reverse reactions. In all the transition states, the reacting C–H bond is significantly extended from its value in $\text{RCH}_2\text{O}_{(\text{ad})}$. The C–O bond lengths and O–C–C bond angles are closer to those of the product of the forward reaction than to those of the reactant. That is, our DFT calculations confirm that the transition states of the forward (reverse) reaction are product-like (reactant-like), in agreement with the transition state character inferred from experimentally observed substituent effects.

The importance of characterizing surface transition states as reactant-like or product-like is that it potentially allows predictions to be made about the sensitivity of surface reactions to their environment. One of us recently proposed that reactions with product-like (reactant-like) transition states are relatively sensitive (insensitive) to their environment. This proposition is consistent with a number of examples in which surface transition states have been systematically characterized [15–20].

The hypothesis above makes a straightforward prediction about β -hydride elimination on metal surfaces, namely, that the E_{act} for the forward reaction should be quite different on different catalysts, but the reverse reaction should be relatively insensitive to the catalyst, provided that the nature of the transition state is similar on all surfaces considered. We can test this idea by comparing computed activation energies for methoxy decomposition, that is, $R = \text{H}$ in Eq. (1), on multiple metal surfaces. We examined this reaction on Cu(111) and found $E_{\text{act}} = 30.9$ (8.3) kcal/mol for the forward (reverse) reaction, in good agreement with previous calculations for this system [17,21] and with experiment [1]. On PdZn(111), Chen et al. reported $E_{\text{act}} = 27.0$ (12.4) kcal/mol for the forward (reverse) reaction [21]. The forward (reverse) barriers on Pt(111) were computed by Greeley and Mavrikakis to be 5.8 (14.6) kcal/mol [17]. On these surfaces, adsorbed methoxy has $d_{\text{C-H}} = 1.1$ Å and $d_{\text{C-O}} = 1.42$ –1.43 Å, while $\text{CH}_2\text{O}_{(\text{ad})}$ has $d_{\text{C-O}} = 1.2$ –1.3 Å. The transi-

tion states on these surfaces are characterized by having $d_{\text{C-H}} > 1.5$ Å and $d_{\text{C-O}} < 1.33$ Å, so all can be described as product-like transition states for the forward reaction. Remediakis et al. examined this reaction on Ni(111), reporting $E_{\text{act}} = 8.3$ (7.6) kcal/mol for the forward (reverse) reaction [22]. Information on the geometry of the transition state was not provided for this system. On these four surfaces, the activation energy for the forward reaction with a product-like transition state varies from 5.8–30.9 kcal/mol. The reverse reaction, which has a reactant-like transition state, has a considerably smaller range of activation energies, 7.6–14.6 kcal/mol. These observations are consistent with the hypothesis stated above in that the rates associated with product-like transition states are correlated with stronger variation between different surfaces than those stemming from reactant-like transition states.

The one additional example in which the transition state for methoxy decomposition has been characterized provides an important caveat to the general hypothesis above. Chen et al. found that the activation energy for the forward (reverse) reaction on Pd(111) is 7.9 (18.6) kcal/mol [21]. The value for the reverse reaction appears to strain the description made above that the activation energy varies only mildly as the catalyst is varied. Examination of the transition state geometry, however, shows that $d_{\text{C-H}} = 1.39$ Å and $d_{\text{C-O}} = 1.33$ Å. These values are the smallest and largest, respectively, of these bond distances observed in any of the methoxy decomposition reactions listed here and it is difficult to classify them as defining a product-like transition state. Hence, the available data for β -hydride elimination in methoxy groups on metal surfaces support the above hypothesis when it is applied to a set of surfaces for which the nature of the transition state is similar.

Our results have concentrated on reactions catalyzed by atomically flat surfaces. Describing reactions in terms of their transition state character should also be a useful means of considering the equally important topic of structure sensitivity among reactions on different types of sites (terraces, steps, kinks, and so on) on a particular catalyst. General rules for understanding this aspect of structure sensitivity have been proposed by Liu and Hu on the basis of DFT calculations for C–H and C–O bond breaking and making reactions [23]. Approaches of this type and of the type we have considered in this letter should find wide applicability in understanding and controlling surface catalyzed reactions.

Acknowledgement

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