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Journal Article

N.B.: When citing this work, cite the original article.

Original Publication:

Jonas Björk , Thermodynamics of an Electrocyclic Ring-Closure Reaction on Au(111), The Journal of Physical Chemistry C, 2016. 120(38), pp.21716-21721.

<http://dx.doi.org/10.1021/acs.jpcc.6b08755>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-131752>

Thermodynamics of an Electrocyclic Ring-Closure Reaction on Au(111)

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Abstract

We have computationally studied the effects of temperature on the reaction pathway of an electrocyclic ring-closure reaction on the Au(111) surface, particularly focusing on thermodynamic aspects of the reaction. The electrocyclic ring-closure is accompanied by a series of dehydrogenation steps, and while it is found that temperature, in terms of vibrational entropy and enthalpy, has a reducing effect on most energy barriers, it does not alter the qualitative appreciation of the reaction kinetics. However, it is found that the way the abstracted hydrogen atoms are treated is crucial for the thermodynamics of the reaction. The overall reaction is highly endothermic, but becomes thermodynamically favorable due to the entropy gain of the hydrogen byproducts, which desorb associatively from the surface as H₂. The study provides new outlooks for the theoretical treatment of reactions related to on-surface synthesis, anticipated to be instructive for future studies.

Introduction

On-surface synthesis has become an increasingly popular strategy to induce chemical reactions, both by interconnecting molecules into covalent nanostructures^{1–11} as well as inducing

single-molecule reactions.¹¹⁻¹⁴ The reactions normally take place on metal surface under ultrahigh vacuum (UHV) conditions. This bottom-up approach comes with several advantageous. In particular, it allows for the formation of insoluble materials with atomic precision, such as ultranarrow graphene nanoribbons.^{4,5}

The on-surface reactions often behave rudimentarily different from their wet chemistry analogues, and it has become customary to computationally study them with electronic structure methods, to gain insight into their reaction mechanisms.^{11,15-23} These studies have almost exclusively been performed at 0 K, excluding even zero-point vibrations, and only a few examples have attempted to include temperature effects.^{11,20} In particular, no studies have addressed the thermodynamics of reactions related to on-surface synthesis. At the same time, it was recently illustrated that such considerations provide great insight into simple dehydrogenation reactions on surfaces, particularly pointing out the importance of taking into account the entropy of the abstracted hydrogen atoms, which potentially desorb associatively as H₂.²⁴ Dehydrogenation reactions, and in particular C-H activation, on coinage metals are usually endothermic by nature,²⁰⁻²³ and their occurrence are often, handwavingly, explained by the desorption of H₂ into the vacuum without further analysis.

Here, we investigate the effect of temperature on an on-surface reaction containing a number of dehydrogenation steps, as well as a C-C coupling step, namely an intramolecular electrocyclic ring-closure (ERC) reaction between terminal ethyl groups on Au(111). The effects of temperature on energy barriers will be considered, in terms of vibrational enthalpy and entropy. Furthermore, we will consider the entropy effects of abstracted hydrogen atoms, as they desorb associatively as H₂ into the vacuum. The purpose of the study is to demonstrate how large the different temperature-contributions are, providing guidelines for which temperature-effects we may want to include in reaction pathway calculations, and which we may not.

A few examples of ERC reactions have been demonstrated on surfaces under UHV conditions, all in which ethyl groups undergo dehydrogenation steps, followed by the ERC

Scheme 1: The mechanism of the reaction illustrated for a model system. The ERC reaction is preceded by four dehydrogenation steps, and followed by the abstraction of two hydrogen atoms.

reaction and additional dehydrogenations. Heinrich *et al.* illustrated how an octaethylporphyrin underwent an ERC reaction to yield a tetrabenzoporphyrin on the Au(111) surface.¹² Furthermore, Cirera *et al.* demonstrated that an octaethyl-tetraazaporphyrin underwent a similar reaction, resulting in phthalocyanine species on the same surface.¹¹ In the latter case, it was also illustrated that the ERC is competing against an intermolecular coupling, tentatively initiated by a [2+2] cycloaddition. Finally, it has been shown that ERC is also feasible on the Cu(100) and Ag(111) surfaces.¹³

Electronic structure theory has provided insight into the intramolecular ERC reaction, and some insight into the competing intermolecular coupling, on Au(111).¹¹ The ERC reaction (illustrated for a model compound in Scheme 1) is enabled by four initial dehydrogenation steps, in which two ethyl groups are transformed into ethenyl. The two ethenyl legs then undergo the actual ring closure step, which is followed by two dehydrogenation steps that finalize the reaction. Although we have a rigid picture for how the ERC reaction proceeds on Au(111), there are important aspects still to be discussed. In particular, we are lacking a thermodynamic description of the reaction, as the prevailing theoretical treatment of the pathway has considered, almost exclusively, only the potential energy (electronic enthalpy) at 0 K, which is the standard procedure in theoretical descriptions of on-surface synthesis (*vide supra*). Calculations have shown that the reaction is highly endothermic, making it appealing to investigate the effect of temperature, to elucidate what drives the reaction from a thermodynamic point of view.

Computational Details

The ERC reaction between ethyl groups, with its accompanying dehydrogenation reactions, is investigated within the framework of transition state theory and periodic density functional theory (DFT) as implemented in the VASP code.^{25–27} Plane waves were expanded to a kinetic energy cutoff of 400 eV. Exchange-correlation effects were described by the van der Waals density functional²⁸ (vdWDF) in the version proposed by Hamada denoted as rev-vdWDF2,²⁹ which has shown to describe adsorption heights with great accuracy on Au(111).³⁰ The Au(111) surface was represented by a four layered slab and a $p(6 \times 6)$ super cell together with a 4×4 k -point sampling. Structural optimizations were performed until the forces on all atoms, except for the bottom two layers of the slab, were smaller than 0.01 eV/Å, both for local minima and transition states. Reaction paths were calculated with the climbing image nudge elastic band and Dimer methods.^{31,32}

To assess the effects of temperature, we will primarily compare two scenarios. In the first, we only take into account the potential energy of the system, *i.e.* the electronic enthalpy H^{elec} , and the energy difference at state $\mathbf{Sx}$ along the path is given with respect to the initial state $\mathbf{S0}$ as

$$\Delta H^{\text{elec}} = H_{\mathbf{Sx}}^{\text{elec}} - H_{\mathbf{S0}}^{\text{elec}} + \frac{1}{2}H_{\text{H}_2}^{\text{elec}}. \quad (1)$$

Here, $H_{\mathbf{Sx}}^{\text{elec}}$ is the electronic enthalpy of state $\mathbf{Sx}$, $H_{\mathbf{S0}}^{\text{elec}}$ is the electronic enthalpy of the initial state $\mathbf{S0}$, n_{H} is the number of abstracted hydrogen atoms in $\mathbf{Sx}$, and $H_{\text{H}_2}^{\text{elec}}$ is the electronic enthalpy of a hydrogen molecule in the vacuum.

In the second scenario, we consider Gibbs free energy of the system at a temperature T , and define the free energy difference of state $\mathbf{Sx}$ with respect to the initial state $\mathbf{S0}$ as

$$\Delta G(T, p) = G_{\mathbf{Sx}}(T) - G_{\mathbf{S0}}(T) + \frac{1}{2}n_{\text{H}}G_{\text{H}_2}(T, p), \quad (2)$$

where $G_{\mathbf{Sx}}(T)$ and $G_{\mathbf{S0}}(T)$ are the free energies of $\mathbf{Sx}$ and $\mathbf{S0}$, respectively, and $G_{\text{H}_2}(T, p)$

is the free energy of a hydrogen molecule in the vacuum at a pressure p . Definitions of the free energy components, and details of how these were calculated, can be found in the Supporting Information (SI). To make the comparison of different free energy components more assessable, we rewrite the free energy difference as

$$\Delta G(T, p) = \Delta H^{\text{elec}} + \Delta H^{\text{nuclei}}(T) - T\Delta S^{\text{vib}}(T) - \frac{1}{2}n_{\text{H}_2}TS_{\text{H}_2}(T, p), \quad (3)$$

where ΔH^{elec} is the electronic enthalpy difference defined by Eq. (1). $\Delta H^{\text{nuclei}}(T)$ is the enthalpy difference due to the movement of the nuclei and $\Delta S^{\text{vib}}(T)$ is the vibrational entropy difference, defined in the SI. Finally, $S_{\text{H}_2}(T, p)$ is the entropy of H_2 at temperature T and gas pressure p , and can be calculated as²⁴

$$S_{\text{H}_2}(T, p) = S_{\text{H}_2}(T, p_0) - k_{\text{B}} \ln \left(\frac{p}{p_0} \right), \quad (4)$$

where k_{B} is Boltzmann’s constant. This term gives the entropy gain due to the associative desorption of hydrogen to the vacuum. We have used tabulated values for the hydrogen gas entropy at the standard pressure $p_0 = 1$ bar.³³

Results and discussion

In the following, we will consider the reaction pathway for the model reaction in Scheme 1, comparing ΔH^{elec} at 0 K and $\Delta G(T, p)$ calculated for $T = 300$ °C and a $p = 10^{-10}$ bar.

Figure 1 depicts the mechanism of the initial four dehydrogenation steps of the reaction. As previously shown, the reaction is most easily initiated by dehydrogenating one of the methylene bridges (**S0–S1**), which has a significantly lower barrier than initially dehydrogenating a methyl group.¹¹ Following the dehydrogenation of a methylene, the barrier for dissociating the corresponding methyl group (**S1–S2**) is reduced, with a barrier smaller than the first dehydrogenation. Following the transformation of one ethyl group into ethenyl, the

second ethyl group undergoes an equivalent two-step process (**S2**–**S4**). With one exception, the free energy barriers are smaller than the electronic enthalpy ones. This is expected given that the transition states have one C-H vibrational mode less than proceeding local minima (for example, **TS1** has one vibrational mode less than **S0**). The most notable result from Figure 1 is, however, that the dehydrogenation steps are endothermic when considering the electronic enthalpy at 0 K, with a reaction energy of 2.52 eV, while they are thermodynamically favorable, with a free energy difference of -1.54 eV between **S4** and **S0**.

Figure 1: Reaction mechanism of the four dehydrogenation steps initiating the reaction, with (a) valence bond structures of local minima, (b) top and side views of the structures of local minima (**S0**–**S4**) and transition states (**TS1**–**TS4**) on Au(111), and (c) electronic enthalpy profile in blue and the free energy profile (calculated at $T = 300$ °C and $p = 10^{-10}$ bar) in red. The green arrows in (b) indicate that the abstracted hydrogens are removed from the system (desorbed as H_2). Units in eV.

The final steps of the reaction are shown in Figure 2. Starting from **S4**, in which both ethyl groups have been transformed into ethenyl, the molecule undergoes the actual ERC reaction (**S4**–**S5**), for which the free energy barrier is smaller by 0.16 eV compared to the potential energy barrier. The ERC is followed by two dehydrogenation reactions (**S5**–**S7**) with

relatively small barriers. Again, the most significant difference between the two scenarios is that the second half of the reaction is only slightly exothermic when considering the electronic enthalpy, while the system gains 2.19 eV in free energy. Furthermore, from Figure 1 and 2 we can conclude that the ERC step has the largest barrier, both when considering the potential energy and the free energy, and is expected to be the rate-limiting step of the overall reaction. Thus, one may expect to observe **S4** in experiments. However, **S4** has not been observed experimentally due to a competing intermolecular reaction, with relatively small activation energy.¹¹ Importantly, although the inclusion of vibrational enthalpy and entropy affects energy barriers quantitatively, they do not alter our qualitative understanding of the reaction kinetics, as the hierarchy between the barriers remains unchanged.

Considering the overall reaction, ΔH^{elec} suggests an endothermic reaction with an overall reaction energy of 2.32 eV, while the overall free energy difference between the final state **S7** and the initial state **S0** is -3.74 eV. It should be noted that the reaction is endothermic also when adding zero-point vibrations to ΔH^{elec} , with an overall reaction energy of 1.43 eV (see SI). Thus, it is clear that it is crucial to include temperature effects to make the reaction thermodynamically favorable, but so far we have not unraveled what are the main contributions lowering the free energy.

To investigate where the free energy gain originates from, we decompose the free energies for each state of the reaction into the contributions given by Eq. (3), as summarized in Table 1. As a general trend, the enthalpy from the nuclei motion ΔH^{nuclei} has a tendency to reduce the free energy. At the same time, the vibrational entropy ΔS^{vib} has an opposite effect, generally increasing the free energy. The net effect is that most energy barriers are slightly reduced, as the effect of ΔH^{nuclei} is larger than that of ΔS^{vib} for most transition states, while they are generally quite similar for local minima. Notably, considering the overall reaction, these two contributions cancel out each other almost perfectly, at the final state **S7**.

Instead, what drives the reaction from a thermodynamic point of view is the entropy

Figure 2: Reaction mechanism of the ERC reaction and the two dehydrogenation steps finalizing the reaction, with (a) valence bond structures of local minima, (b) top and side views of the structures of local minima (**S4–S7**) and transition states (**TS5–TS7**) on the Au(111) surface, and (c) electronic enthalpy profile in blue and the free energy profile (calculated at $T = 300$ °C and $p = 10^{-10}$ bar) in red. Notice that the blue and red curves have been moved closer together to minimize the amount of white space in the figure, which makes the energy difference between the two curves appear too small. The green arrows in (b) indicate that the abstracted hydrogens are removed from the system (desorbed as H_2). Units in eV.

of the abstracted hydrogen atoms that desorb from the surface as H_2 . At the conditions $T = 300$ °C and $p = 10^{-10}$ bar, each split-off hydrogen atom contributes with roughly -1 eV to the free energy due to the entropy of H_2 in the vacuum, which sums up to a significant free energy gain considering the six dehydrogenation steps of the reaction. In other words, for studying the thermodynamic aspects of this particular reaction, it appears sufficient to add the entropy of the hydrogen gas to the electronic enthalpy. This is a quite appealing approach for many problems, as the entropy of the hydrogen gas is added simply as an empirical correction, which does not add to the computational effort, while computing vibrational enthalpies and entropies requires quite a significant additional effort, even at the

Table 1: Decomposition of the free energy into its different contributions, as defined by Eq. (3). Units in eV.

	ΔH^{elec}	$\Delta H^{\text{nuclei}}(T)$	$-T\Delta S^{\text{vib}}(T)$	$-\frac{1}{2}n_{\text{H}}TS_{\text{H}_2}(T, p)$	$\Delta G(T, p)$
S0	0.00	0.00	0.00	0.00	0.00
TS1	1.36	-0.18	0.10	0.00	1.28
S1	1.08	-0.13	-0.05	-1.01	-0.11
TS2	1.77	-0.30	0.15	-1.01	0.61
S2	1.21	-0.21	0.29	-2.03	-0.74
TS3	2.71	-0.43	0.30	-2.03	0.55
S3	2.47	-0.33	0.22	-3.04	-0.68
TS4	3.11	-0.48	0.28	-3.04	-0.13
S4	2.52	-0.43	0.42	-4.05	-1.54
TS5	4.34	-0.51	0.34	-4.05	0.12
S5	2.81	-0.45	0.60	-4.05	-1.09
TS6	3.40	-0.59	0.44	-4.05	-0.80
S6	2.89	-0.59	0.52	-5.07	-2.25
TS7	2.94	-0.69	0.61	-5.07	-2.21
S7	2.32	-0.62	0.64	-6.08	-3.74

level of the harmonic approximation.

It should be noted that, due to their temperature dependence, $\Delta H^{\text{nuclei}}(T)$ and $-T\Delta S^{\text{vib}}(T)$ will not always cancel out each other. Figure 3 illustrates how $\Delta H^{\text{nuclei}}(T) - T\Delta S^{\text{vib}}(T)$ between the final state **S7** and the initial state **S0** depends on the temperature. Naturally, at 0 K the entropy is zero, while $\Delta H^{\text{nuclei}}(T)$ is non-zero due to zero-point vibrations. As the temperature increases, $-T\Delta S^{\text{vib}}(T)$ becomes more prominent, and around 560 K the two contributions cancel out each other, very close to the experimental conditions of the reaction (300 °C = 573.15 K). At lower temperatures, the effect of the combined effect of $\Delta H^{\text{nuclei}}(T)$ and $-T\Delta S^{\text{vib}}(T)$ is quite significant, and it would be of great interest to investigate their role for similar reactions taking place at lower temperatures, in particular as the entropy of desorbing hydrogen is smaller under such conditions.

It is evident that the entropy of the associatively desorbed hydrogen is crucial for making the overall reaction thermodynamically favorable. However, it is not clear from these data under what conditions we may expect the reaction to be favorable from a thermodynamic point of view. To shine some light on this, we calculated the free energy difference between

Figure 3: The contribution of $\Delta H^{\text{nucl}}(T) - T\Delta S^{\text{vib}}(T)$ to the free energy as a function of the temperature.

the final state **S7** and initial state **S0** for different gas pressures p and temperatures T , using Eq. (3). The results are plotted in Fig. 4. At pressures of $10^{-12} - 10^{-10}$ bar, typical for UHV experiments, the reaction is thermodynamically favorable already below 200 K. Given that the reaction occurs experimentally around 300 °C¹¹ indicates that it is the kinetics rather than the thermodynamics of the system that restricts the reaction to occur at lower temperatures. In other words, to make the reaction happen at lower temperatures, we need to reduce the energy barriers. It is also interesting to notice that the reaction is thermodynamically favorable at relative high gas pressures for $T = 300$ °C, indicating the possibilities of inducing the reaction outside the UHV chamber, at least under a pure hydrogen atmosphere.

Conclusions and Outlook

In conclusion, we have computationally studied an ERC reaction on Au(111) including different temperature effects. While the combined effect of vibrational enthalpy and entropy in general lowers the energy barriers, their inclusion do not have a qualitative effect on the reaction pathway. The overall reaction is considerably endothermic, and is thermodynamically driven by the entropy gain of split-off hydrogen atoms that desorb from the surface associatively as H_2 .

As a final remark, for the theoretical modeling of chemical reactions on surfaces we need

Figure 4: Free energy difference between the final state **S7** and initial state **S0** as a function of temperature and pressure of the hydrogen gas. The solid black line shows where the free energy difference is zero, and the dashed green line indicates $T = 300$ °C, at which the reaction has been observed experimentally.¹¹ The reference pressure p_0 is 1 bar.

to balance the accuracy of our theoretical framework with the number of reactions we will be able to compute. We can either aim for detailed descriptions of individual reactions, as in the current study, or we can systematically study reactions for a larger selection of molecules and surfaces but with a less sophisticated theory. The latter option is maybe the most appealing one in most cases, and would allow theory to provide insight how reactions are governed by the choice of molecule and surface, with the potential of aiding the design of new on-surface synthesis protocols with particular reaction patterns. In either case, a simple inclusion of the entropy of split-off hydrogen atoms is instructive for understanding fundamental thermodynamic aspects of reactions, which may well be the case also for on-surface reactions with other reaction byproducts.

Acknowledgement

Computer recourses were allocated by the National Supercomputer Centre, Sweden through SNAC.

Supporting Information Available

Details about free energy contributions and how these were calculated, as well as additional figures are provided in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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