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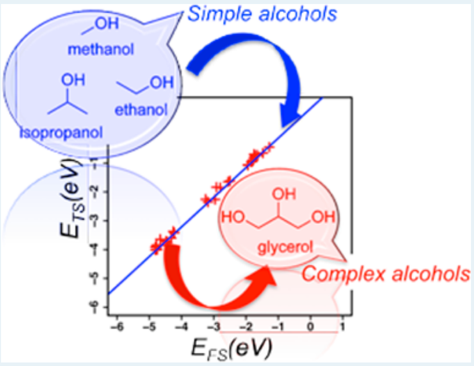
Linear Energy Relations As Predictive Tools for Polyalcohol Catalytic Reactivity

Jérémie Zaffran, Carine Michel, Florian Auneau, Françoise Delbecq, and Philippe Sautet*

Université de Lyon, CNRS and Ecole Normale Supérieure of Lyon, 46 Allée d'Italie, 69364 Lyon Cedex 07, France

Supporting Information

ABSTRACT: Molecules extracted from biomass can be complex, and computing their reactivity on a catalyst is a real challenge for theoretical chemistry. We present herein a method to predict polyalcohol reactivity in heterogeneous catalysis. We start from a set of simple alcohol molecules, and we show that an accurate linear energy relationship can be constructed from DFT calculations for the O−H and C−H dehydrogenation reactions. We then show that this relation can then be used for a fast prediction of the reactivity of glycerol. Compared with pure DFT calculations, our method provides results of good accuracy with a systematic deviation of ~0.1 eV. We were able to prove that this deviation is caused mainly by intramolecular effects occurring in glycerol and not in simpler molecules.



KEYWORDS: *Brønsted−Evans−Polanyi type relationships, glycerol, polyols, biomass, monoalcohols, dehydrogenation, DFT*

Molecules extracted from biomass set new challenges for heterogeneous catalysis and require the design of improved catalysts.[1,2] The cellulosic fraction of biomass is constituted of polyalcohols, which can be transformed to valuable products (chemicals or fuels) by various types of chemical reactions (dehydrogenation, hydrogenolysis, dehydration, ...).[3] These polyalcohols are associated with a large space of geometric configurations, and they can be involved in a complex network of serial or parallel reactions, which render the study of their reactivity with a solid catalyst complex and tedious. The calculation of their reactions at metal surfaces requires quantum chemical methods to properly describe bond-breaking and bond-forming steps, but these methods are too heavy for a fast exploration of complex reaction networks. It is hence of utmost importance to design methods that are of similar accuracy to quantum chemical approaches but can allow a fast screening of multiple elementary steps.

In this work, we show that transition state energies and reaction barriers for polyalcohols can be efficiently predicted from linear relationships of Brønsted−Evans−Polanyi (BEP) type, linking the desired kinetics quantities with more easily accessible adsorption energy or reaction energy data, which are established here using a set of monoalcohol molecules. Here, we use glycerol as a prototype polyalcohol, and we focus on dehydrogenation reactions on a Rh catalyst, hence involving the C−H and O−H bond-breaking processes. Indeed, it has been demonstrated that dehydrogenation is the first step for glycerol transformation on a Rh catalyst, under H_2 gas pressure or under He.[4] Even if one restrains the reactivity of glycerol to dehydrogenation processes, many pathways are possible by a combination of elementary acts dealing with CH/OH groups in central/terminal positions. In addition, glycerol can adopt a very large number of configurations in the gas phase[5] and on a surface.[6] It is unclear if the most stable configuration will be the most reactive one, and probing all configurations/pathways with first principle approaches such as DFT is, hence, a very tedious and computer-intensive task.

The idea of simple and fast evaluation of activation barriers from reaction thermodynamic data traces back to the pioneering work of Brønsted,[7] Bell,[8] Evans, and Polanyi,[9] as detailed in a recent review.[10] These correlations were initially used to compare molecular reactivity and, in a later stage, to model the kinetics of chemical reactions. They have been applied to heterogeneous catalysis reactions by several authors; however, two alternative methods were considered. Although some authors correlated activation energy with reaction energy,[11−14] in a traditional BEP style, others proposed to correlate the transition state energy with the energy of the initial or the final state of the reaction, a method later referred to as transition state scaling (TSS).[15−19] Only a few papers compare the merits of both correlation methods.[20,21] The situation remains confused on this point because for a single type of correlation, different definitions were used. In this paper, we will explore both TSS (with eight possible definitions) and BEP (with four definitions) correlations to clarify their comparison.

A general catalytic elementary step is shown in Scheme 1. The step starts from the initial state minimum, IS; progresses through the transition state, TS; and finishes at the final state

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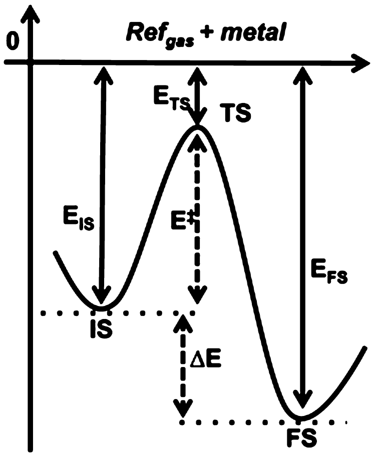
Scheme 1. General Scheme of a Surface Catalytic Elementary Step[a]

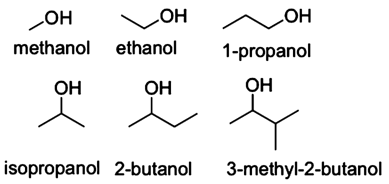


[a] E_{TS}, E_{IS}, and E_{FS} are energies of the transition state, the initial state, and the final state, respectively. $E^{\ddagger}$ and ΔE are activation and reaction energies, respectively.

minimum, FS. The principle of the BEP analysis is to explore the correlation behavior when plotting the activation (or the TS) energy versus the reaction (or FS) energy for a given sample of such reaction steps. The definition of IS and FS is not absolute because it depends on the direction chosen for the reaction. In our case, one can define the direction from the reaction itself, bond dissociation (diss), or association (assoc). Another possibility is to select the direction on an energy criterion, such as for each step choosing the endothermic (endo) or exothermic (exo) direction. This defines four types of BEP analysis, expressing the correlation between the activation energy, $E^{\ddagger} = E_{TS} - E_{IS}$, and the reaction energy, $\Delta E = E_{FS} - E_{IS}$. TSS relations correlate intrinsic TS and FS energies so that a reference energy is needed. We use as a reference a state in which all surface fragments are considered in gas phase, and the most stable spin state was chosen in the case of radicals. A TSS relation is, hence, defined by a direction (diss/assoc or exo/endo), a choice of thermodynamic state (either IS or FS), and a choice for the energy reference (again IS or FS). Our general notation is diss.IS/IS, where the last symbol defines the energy reference. Clearly, diss.IS/IS and assoc.FS/FS are identical definitions, such as exo.FS/FS and endo.IS/IS, so that only diss and exo directions will be kept. Eight types of TSS are then defined.

The existence and the quality of the correlation will be studied on a sample of simple alcohol molecules that are displayed in Scheme 2. Six molecules have been chosen with several substitution levels and a mixture of primary and secondary alcohols. For each of them, OH and CH bond dissociations have been considered, with a further distinction between CH bonds in the α or β position with respect to the OH. First and second dehydrogenation reactions have been considered so that a set of dehydrogenated products is formed of various chemical natures (radicals, carbonyls, enols). In total, the sampling set contains 29 bond activations (12 CHα, 7 CHβ, and 10 OH, see the Supporting Information (SI)).

Scheme 2. Sample of Molecules Used to Establish the BEP Type Relationships[a]



[a] Here are depicted the six monoalcohol molecules generating the 29 elementary CH and OH dissociation steps included for the construction of the linear relations.

If we first select the diss.FS/FS, exo.FS/IS, and BEP.diss forms of correlation, which have been previously used in the literature,[11−21] the 29 points E_{TS}/E_{FS} or $E^{\ddagger}/\Delta E$ are displayed in Figure 1. A clear and high-quality linear relation is seen. The statistical analysis of the deviations between DFT values and linear relation values are shown for each correlation as box plots on the inserts of Figure 1. We also report the mean absolute error (MAE) and the maximum error (MAX). Error is defined as "DFT value − linear relation value". The three chosen correlation definitions give very similar error distributions for the three subsets CHα/CHβ/OH, in a range from ∼−0.1 to +0.1 eV. This attests to the good quality of these relationships, which is confirmed by a MAE on the order of 0.05 eV (see Table 1) in each case. Note that the range of data is smaller for the BEP definition, giving a less visually appealing correlation (and a larger confidence interval for the slope of the linear relation; see the SI) for a similar distribution of errors. Let us highlight in addition that splitting the sample into three subsets considerably lowers the errors of the linear model, as shown by the MAE/MAX analysis, which is almost divided by 2. Furthermore, predicting CHα/CHβ/OH by a model established with all the points together leads to nonnegligible systematic errors (see SI Figure S2), significantly degrading the prediction.

From this analysis of the sampling set, the three selected types of correlations are of equivalent and high quality, and the error values after a separation in the three types of bonds is small (MAE ∼ 0.05 eV), which is very encouraging for a use of these correlations in predicting reactivity. A similar result was obtained for all 12 types of correlations considered, as seen in Figure 2. When taking all bonds together, only small variations are seen in the MAE between the methods, and hence, all 12 should be evaluated as being of the same general quality (error ∼ 0.08 eV). Separation of the set in each type of dissociated bond (CHα/CHβ/OH) again lowers the error, showing fluctuations around 0.05 eV for the various methods. None, however, is consistently better than the other ones, even if for the specific case of CHβ dissociation BEP are more accurate than TSS (for box plots, see SI Figure S3). The main point here is to clearly stress that TSS and BEP type relations have a similar (and high) merit,[19] at least for Rh catalysts and the chosen family of monoalcohol molecules.

Our results also show that the choice of the direction of the reaction (either on a chemical or energy base) or of the reference (for TSS modes) is not determinant for the result. This is, of course, reassuring for the robustness of the correlation concept and its usage for a wide range of systems and reactions. The BEP formulation has some practical advantages because the correlated quantities are more directly linked with reaction thermodynamics and kinetics so that trends can more clearly be caught and so that the slope (also called the transfer coefficient) has a simple interpretation in terms of early or late character of the transition state.

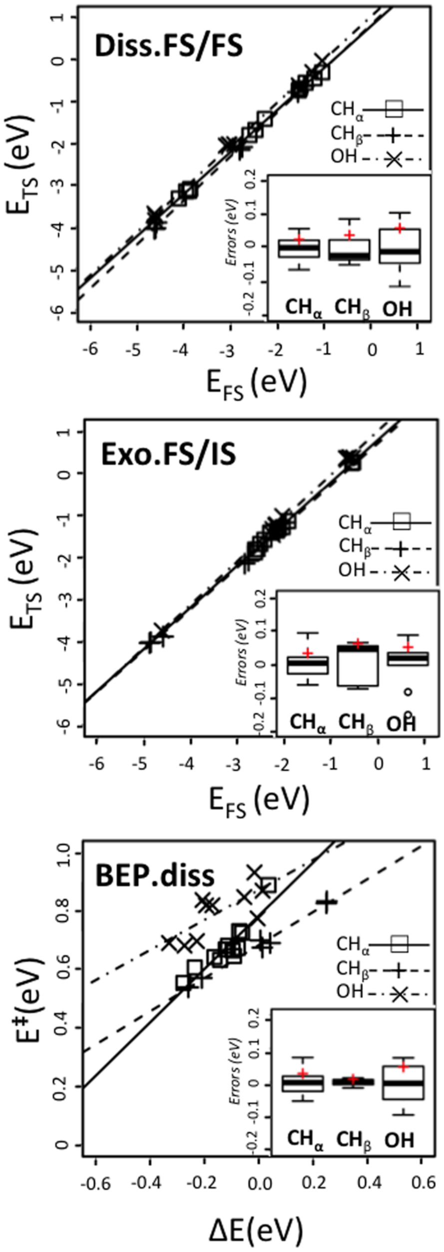


Figure 1. Linear relations constructed from first and second dehydrogenation steps of the six monoalcohol molecules of Scheme 1 on Rh(111). Three definitions of the correlation are considered: □, ×, and + are the DFT calculated values for CHα, CHβ, and OH respectively; and full, dashed, and mixed lines are the corresponding linear relations. At the bottom right corner of each graph, the box plots depict the corresponding error distribution. Red crosses signal mean absolute errors (MAE).

Now that we have established these correlations on the monoalcohol sample set, we turn to the central question: Can we use them to predict the reactivity of glycerol, chosen as a prototype polyalcohol? We have considered all first and second C−H and OH bond dissociations of glycerol on Rh(111). Note that in the case of glycerol, all CH bonds are in α of an OH group. For simplicity, we focus here on only the three correlation modes already selected for Figure 3 (diss.FS/FS, exo.FS/IS, and BEP.diss), but a complete analysis is provided in the SI (see Figure S4). We calculated the most stable initial and final states for first and second hydrogenation processes on glycerol on Rh(111) and determined the TS linking them. Note that for some reaction steps, we included several TS and their corresponding reactants and products (associated with different conformations of glycerol) to improve the reliability of our statistical analysis (see glycerol structures in the SI and Figure S5).

Table 1. Error Analysis for Monoalcohol BEP Type Relationships[a]

	TSS-diss.FS/FS		TSS-exo.FS/IS		BEP.diss	
	MAE	MAX	MAE	MAX	MAE	MAX
all	0.09	0.23	0.08	0.17	0.07	0.18
$CH_α$	0.03	0.06	0.03	0.09	0.03	0.07
$CH_β$	0.04	0.09	0.06	0.07	0.01	0.02
OH	0.06	0.11	0.05	0.15	0.05	0.10

[a] Here is presented the error analysis (mean absolute error, MAE; maximal absolute error, MAX) for the 29 CH and OH dissociation elementary steps of the considered monoalcohols family on Rh(111). The correlation can be established from the global sample (all), or subfamilies can be considered for each type of chemical bond activated (CHα, CHβ, OH).

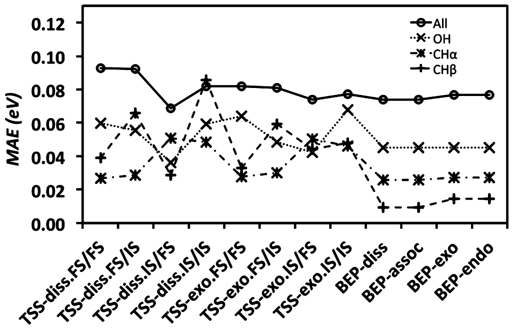


Figure 2. Comparison of the 12 considered definitions for the correlations (grouped into 8 TSS and 4 BEP types). MAE is given for the linear relation considering the 3 subsets (CHα/CHβ/OH) separately and the whole set ("All") of monoalcohol dehydrogenation reactions.

The 31 (18 C−H and 13 O−H dissociations) points for glycerol are shown in Figure 3, together with their associated linear relation in black and with the correlation lines previously established for the monoalcohol family (in red). This graph clearly shows that the correlation established with the monoalcohol family is already a good model to predict the transition state energy or the activation energy for glycerol. The analysis of the deviation between the points for glycerol and the (red) line from the monoalcohol family quantifies this result (see box plots in Figure 3 and Table 2).

Notice that in this case, we also present the mean signed error (MSE), which is nonzero here because the linear relation is not associated with the sample considered for glycerol. One can clearly notice a systematic deviation, the prediction line underestimating the activation energy (on average, by 0.1 eV) for the CH bonds and overestimating it (by 0.1 eV) for the OH bonds. We will see the consequence of this systematic error on the predictive potential of the method later. The MAE is very close to this MSE and, hence, remains small (~0.1 eV for all three definitions). The error is, hence, reasonably increased with respect to the sampling set, and this gives predictive power to the approach. Points corresponding to metastable configurations of glycerol follow the linear relation within given statistical errors, although the most stable thermodynamic state

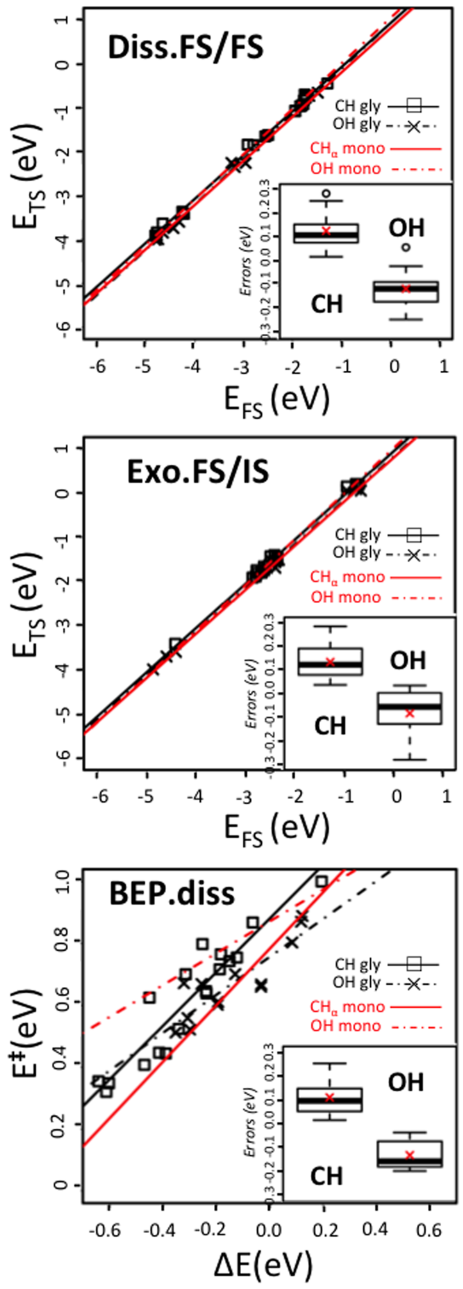


Figure 3. Linear relations constructed from first and second dehydrogenation steps of glycerol on Rh(111). Three definitions of the correlation are considered: □ and × are the DFT calculated values for CH and OH bonds, respectively, and full and mixed lines are the corresponding linear relations. In red are recalled the linear relations obtained in the case of the monoalcohol set for the CHα (full line) and the OH (mixed line) bonds. At the bottom right corner of each graph, the box plots depict the corresponding error distributions between the data points and the (red) monoalcohol linear relations. Red crosses signal mean signed errors.

is not always strictly associated with the most stable TS (see Figure S5 in the SI). Again, the two TSS and the BEP approaches have a very similar performance in terms of error. This can be generalized to all 12 correlation types considered in this paper, as shown in Figure S4 in the SI. All definitions give a similar error distribution, with an especially narrow range for the BEP case for OH dissociation and a larger error for the TSS involving the initial state as variable for the CH activation.

The capability to reasonably predict the catalytic reactivity of glycerol from that of simple alcohols is not a straightforward result, and it opens several perspectives. Generally speaking, to our knowledge, the use of BEP-type relations on simple molecules to predict multifunctional ones has not been demonstrated. It has been proposed, however, to predict the influence of substituents in the case of the hydrogenation of unsaturated aldehydes.[22] There are many reasons why glycerol reactivity might be different from that of simple alcohols. The presence of terminal and central OH/CH is equivalent to primary and secondary alcohols, both of which are in the sampling set. One key difference, however, is the presence in glycerol of intramolecular hydrogen bonds that assist the OH dissociation for the H bond acceptor OH.[23] The DFT-calculated TS energy will, hence, be lower for glycerol than for the monoalcohol sample, hence explaining the ∼-0.1 eV systematic error. This effect appears clearly if one considers some water-assisted reactions in the case of dehydrogenation of monoalcohols.

As a simpler H-bonded system, we considered ethanol, interacting with a chemisorbed water molecule through a H-bond, ethanol being the H-bond acceptor.[22] In this configuration, the OH bond scission in ethanol is modified, and the corresponding points are shifted toward the glycerol line in the BEP plots (see Figure S6 in the SI). In contrast, the positive systematic error seen for the CH bond dissociation is not related to the H bond effect. It stems from the constraints that neighboring OH groups in glycerol exert on glycerol. By interacting with the metal surface, they make the adsorbed molecule more rigid; hence, hindering the formation of the optimal C−H transition structure and increasing its energy with respect to the freer situation of monoalcohol sample. However, these effects are not very marked, and on average, the predictive potential remains good.

In the following, we will consider some examples of glycerol dehydrogenation elementary steps focusing on selectivity issues, that is, on the comparison of the barriers between different paths from a given intermediate. This is a severe test in situations for which DFT barriers are close and will highlight the cases in which a prediction is valid and those for which the accuracy might be insufficient. Scheme 3 presents two examples for glycerol or its hydrogenated intermediate on a Rh(111) surface and compares DFT calculated barriers (below arrow) with those predicted by three correlations built from the monoalcohol family (above arrows). The comparison between CH and OH dissociation (first line) is especially difficult because the systematic deviation in the prediction is different, with an overestimation for OH and an underestimation for CH, and because here, the DFT barrier difference is small. The method is, hence, not able to correctly grasp the preferred reaction.

The second elementary reaction starts from dehydrogenated glycerol at the terminal carbon and compares two further OH dissociation steps. The systematic deviation is eliminated because similar reactions are compared and the random error remains, which is inherent to any statistical model. Errors range now between ∼-0.1 and ∼+0.1 eV, which is similar to the results obtained for simple alcohols. In addition, the difference between barriers obtained from the correlations (0.13−0.22 eV) being large enough to safely predict that the reaction on the right, forming glyceraldehyde, is favored.

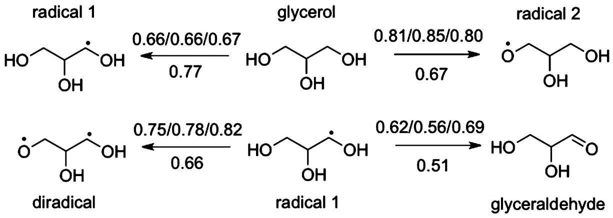
We, hence, showed that linear energy relations established for a sample of monoalcohol molecules on Rh can efficiently be

Table 2. Error Analysis for the Prediction of Glycerol Reactivity[a]

	TSS-diss.FS/FS			TSS-exo.FS/IS			BEP.diss		
	MSE	MAE	MAX	MSE	MAE	MAX	MSE	MAE	MAX
CH	+0.13	0.13	0.28	+0.13	0.13	0.29	+0.11	0.13	0.25
OH	−0.11	0.12	0.24	−0.09	0.10	0.28	−0.13	0.13	0.20

[a] Here is presented the error analysis for predicting glycerol reactivity on Rh(111) from the monoalcohol linear energy relationship using the three main definitions: MSE, mean signed error; MAE, mean absolute error; and MAX, maximal absolute error.

Scheme 3. Prediction of Activation Energies for Glycerol Dehydrogenation[a]



[a] The first line describes two possible paths for the first dissociation starting from glycerol, and the second line describes two probable routes for the second step starting from "radical 1". The value below each arrow is the activation energy predicted by DFT, and the three values above are the activation energies predicted from three definitions of the monoalcohol linear energy relationship (TSS-diss.FS/FS, TSS-exo.FS/IS, BEP.diss).

applied to the prediction of reaction barriers for polyalcohol molecules, such as glycerol with a statistical mean absolute error of ∼0.1 eV. Coupled with other approaches that simplify the evaluation of the adsorption energy of large molecules, as group additivity[24] or scaling relations,[25] this opens a fast and powerful exploration of the complex mechanisms and of the kinetics for the catalytic transformation of molecules extracted from biomass. Small deviations occur from the presence of intramolecular H bonds in the polyalcohol molecule, underestimating (respectively overestimating) the barrier for CH (respectively OH) and, hence, favoring CH dissociation versus OH in the predicted values. It would be certainly important to develop methods to estimate this systematic deviation between the set of CH or OH dissociation steps for glycerol versus monoalcohols because this would allow us to implement a correction on the data and to improve the prediction when comparing dehydrogenation at CH and OH on the polyalcohol. Although this analysis has been performed on a Rh(111) surface, the conclusions should not be specific to that system and extend to other faces or metal, as already proposed for other reaction steps.[18,20] Immediate perspectives aim at generalizing this behavior to other bond cleavages, such as C−C or C−O; other metals; and other types of molecular systems extracted from biomass, such as lignin.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational methods and elements of statistics, additional tables and schemes, list of reactions and their corresponding structures used to get the relationships. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: philippe.sautet@ens-lyon.fr.

Notes

The authors declare no competing financial interest.

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