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A Theoretical and Computational Analysis of Linear Free Energy Relations for the Estimation of Activation Energies

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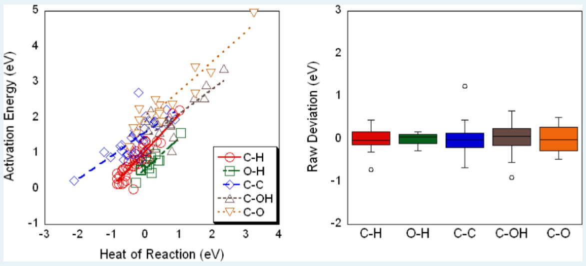
S *Supporting Information*



ABSTRACT: We present a theoretical and computational analysis to elucidate the relation of the Brønsted−Evans−Polanyi (BEP) and transition state scaling (TSS) correlations. We find that the TSS correlation is an approximation of the BEP correlation. The BEP correlation allows for the straightforward identification of homologous series via standard statistical tests and has better error properties than the TSS correlations. We find that the unit cell size used in the DFT calculations does not have a significant effect on the correlation parameters; however, the zero point energy correction does have a significant effect on the correlation parameters, especially for (de)hydrogenation reactions. We propose a method for using this information to estimate zero-point-energy-corrected activation energies without resorting to calculations of the zero point energy correction for every species. Finally, we find that BEP correlations derived for one parent molecule may be applicable to other molecules beyond the training set.

KEYWORDS: *Brønsted−Evans−Polanyi, transition state scaling, homologous series, error, linear free energy relations, BEP*

1. INTRODUCTION

Rational catalyst design has recently emerged as an increasingly important field of study in the hopes that novel, more effective catalyst formulations can be identified with a minimum expenditure of resources.[1−5] Central to most computational approaches is microkinetic modeling.[6] Reasonable estimates for microkinetic model parameters are typically obtained via density functional theory (DFT) calculations. Unfortunately, the calculation of every parameter for microkinetic models of increasingly complex molecules and reactions is prohibitively expensive. Hierarchical multiscale modeling has been proposed as an effective means of addressing this difficulty.[7,8] Recognizing that the majority of parameters in a microkinetic model are unimportant, semiempirical methods can be employed to generate initial approximations for every parameter.[8] Semiempirical techniques, which have been utilized for the estimation of model parameters, include group additivity[9,10] and scaling relations[10−13] for adsorption energies and Brønsted−Evans−Polanyi (BEP) type relations[14−20] for activation energies. After performing initial simulations, the most sensitive parameters can then be identified and refined via DFT.[20−22]

Although sound in principle, this approach depends on adequate initial approximations for the pre-exponentials and activation energies. Microkinetic model predictions are much more sensitive to changes in activation energies than to changes in pre-exponentials because the rate depends exponentially on the activation energy but only linearly on the pre-exponential. Further, although the usual order of magnitude approximations for pre-exponentials are typically adequate, provided thermodynamic consistency is maintained,[21−23] BEP correlations may show significant deviations. BEP type correlations have inherent assumptions by their nature. Yet, they have been useful in applications, and because they are increasingly used in the literature, it is vital that we (1) understand what assumptions are being made and (2) determine the error that can be expected in the resulting estimates.

BEP type correlations were initially proposed by Brønsted,[24] Bell,[25] and Evans and Polanyi[26] for homogeneous chemistries. An excellent review of the theory underlying such correlations was recently published by van Santen, Neurock, and Shetty.[19] For many years, the principal use of such correlations was to compare the reactivities of molecules in a homologous series. In this context, these relations are typically referred to as Bell−Evans−Polanyi relations.[27] It was not until much later with the work of Klein and co-workers,[28,29] among others, that such correlations were successfully used in the modeling of homogeneous kinetics. Following this pioneering work, BEP type correlations were subsequently applied to heterogeneous catalytic reactions. To the best of our knowledge, the first such application was by Pallassana and Neurock,[14] who correlated the activation energies of ethyl and ethylene species on pseudomorphic Pd overlayers with the corresponding heats of reaction in exactly the same fashion as the traditional BEP

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correlation. Liu and Hu were among the first to investigate the relationship of the transition state structure and the BEP correlation for heterogeneous catalysis.[30] Shortly after this development, Alcala et al.[15] proposed an alternate BEP form correlating the transition state energy with the final state energy. This has recently been referred to as a transition state scaling (TSS) correlation.[31] Further work on developing BEP and TSS correlations is summarized in Tables 1 and 2.

Table 1. Literature Sources Reporting BEP Correlations

bond types	parent species	source
C−C	ethanol	32
C−H	ethane	14,33
C−H	acetylene, propyne	34
C−H	methane	35
C−H	ethanol	32
C−N	CN	36
C−N	methylamine	37
C−O	CO_2	38,39
C−O	COOH	39
C−O	CO	36,40
H−H	H_2	39
N−O	NO	41
O−O	O_2	41
O−H	H_2O	39,42
O−H	OH	39,43
O−H	COOH	39
O−H	ethanol	32
C−C, C−N, C−O, O−O	ethane, CN, CO, O_2	16
C−H, N−H, O−H, S−H	methane, ammonia, methanol, H_2O, H_2S	16
C−O, N−N, N−O	CO_2, N_2O, NO_2	16
C−O, N−O, N−N	CO, NO, N_2	44

Some of this prior work has shown that the correlation parameters depend strongly on the training data. Liu and Hu have shown for CO dissociation on several close-packed metals that the slope depends on which row of the periodic table the metal is in.[30] Nørskov and co-workers have also shown with N_2 dissociative adsorption that the intercept depends on the metal facet.[54,58] On the other hand, Wang and Liu found that the correlation parameters depended very little on the metal facet in their study of ethanol oxidation on Pt(111) and Pt(211).[32] In later work on ethane hydrogenation and hydrogenolysis on Pt(111) and Pt(211), Chen and Vlachos[33] also found that both hydrogenation and C−C cracking reactions were relatively insensitive to the metal facet. Most recently, further work by Nørskov and co-workers suggests that the parameters will not vary much for late transition metals.[31,48] In light of this past work, a theoretical study of the dependence of the correlation parameters on the metal and parent molecule would be interesting and should be undertaken. In this paper, we focus our attention on reactions on Pt(111) as a first step by comparing the various BEPs rather than studying the effect of facet or metal on the BEPs.

Even with all the work that has been performed recently, there are still a number of outstanding questions regarding both types of correlations. In this paper, we address a number of topics; namely, (1) the theoretical relationship between the two correlation types, (2) the definition of a homologous series for the purposes of deriving correlations, (3) the expected level of agreement between DFT results and correlation estimates, and (4) the effects the computational method, rigor, or both have on the resulting correlation parameters. To our knowledge, this is the first time that statistical analysis of these correlations and comparison between them have been done.

Table 2. Literature Sources Reporting TSS Correlations

bond types	parent species	source
C−C	ethane	33
C−C	ethanol	32,45,46
C−C	glycerol	47
C−C	ethane, propane	48
C−H	ethanol	32,45,46
C−H	acrolein	49
C−H	methyl acetate	50
C−H	methanethiol	51
C−H	methane, ethane	31
C−N	methylamine	48
C−O	CO_2	52
C−O	ethanol	45,46
C−O	methyl acetate	50
C−O	methanol	48
C−S	methanethiol	51
N−H	ammonia	31,53
N−N	N_2	48,54,55
N−O	NO	48,56
O−H	ethanol	32,46
O−H	H_2O	31
O−O	O_2	48,52
S−H	methanethiol	51
C−C, C−O	ethanol	15,18
C−H, O−H	methanol	57
C−H, O−H	glycerol	47
C−O, N−O, N−N, O−O	CO, NO, N_2, O_2	58

2. METHODOLOGY

To address the questions postulated in the Introduction, we designed a series of systematic DFT calculations and carried them out using the SIESTA DFT code.[59] Specifically, our calculations covered three possible effects: unit cell size (2 × 2 and 3 × 3 cells), zero point energy correction, and parent molecule type (methane, methanol, ethane, ethanol, and ethylene glycol). All reactions were for thermal decomposition on Pt(111) and consisted of dehydrogenation (C−H and O−H) and cracking (C−C and C−O) reactions. Calculations for ethanol were carried out on 2 × 2 unit cells. A subset of the ethanol calculations was repeated on 3 × 3 unit cells. All calculational parameters and methods (pseudopotentials, functional, k-point meshes, convergence criteria, basis sets, transition state search algorithm, etc.) follow the procedure used previously by our group.[33,60] Previously published results for methane and ethane[33] and ethylene glycol[60] as well as some methanol and ethanol results that are in preparation[61] are included here for comparison. The raw energies used in the correlations and error estimates are included in the Supporting Information. Unless otherwise noted, the initial, transition, and final state energies are all binding energies calculated with respect to the clean slab and the reactant in the gas phase. Decomposition products were adsorbed on separate slabs.

Correlation parameters were obtained via ordinary least-squares linear regression. The 95% confidence intervals for the parameters were calculated using standard definitions.[62] The statistical independence of correlations was determined by comparing the estimated coefficients via their 95% confidence intervals. The agreement between correlation estimates and the underlying DFT data was examined by calculating the raw deviation between the DFT value and the correlation estimate. Similarly, the deviations due to change in cell size and presence of zero point energy correction were calculated. Distributions of the deviations were analyzed via box plots (a brief explanation of these is given in the Supporting Information). All statistical calculations and regressions were carried out in MATLAB.[63]

3. RELATIONSHIP BETWEEN THE BEP AND TSS CORRELATIONS

An important issue to explore is the relationship between the two correlation types either for a given type of surface (e.g., close-packed Pt) or for a given adsorbate (e.g., adsorbed ethanol, but not its derivatives). In the discussion that follows, the correlations are restricted to reactions of multiple adsorbates on Pt(111), but it is expected that the same treatment will apply when holding the adsorbate constant and varying either the metal composition or the type of surface facet (e.g., terraces, steps, kinks, etc.).

The functional forms of the BEP and the TSS correlations are

$$\hat{E}_A = \alpha \Delta H + \beta \tag{1}$$

$$\hat{E}_{TS} = \alpha' E_{FS} + \beta' \tag{2}$$

The energy definitions are given in Figure 1. The hats on the activation energy and transition state energy terms indicate that these values are estimates rather than actual DFT values. If we fix the values of the initial and final state energies, then estimating the activation energy and the transition state energy are mathematically equivalent. By writing a reaction in the reverse direction, the TSS correlation can also be put in terms of the initial state energy. Figure 2 provides an example of each of the correlation types for reference.

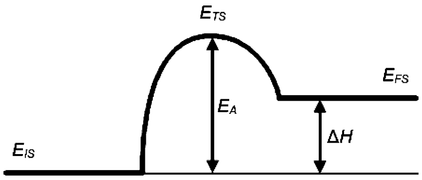

Figure 1. Energy definitions in the BEP and TSS correlations. The key energies in each elementary reaction are the initial state energy E_{IS}, the transition state energy E_{TS}, the final state energy E_{FS}, the heat of reaction ΔH, and the activation energy E_A. In the case of the initial, transition, and final state energies, these may be calculated with respect to an arbitrary reference.

To determine how the coefficients of the two correlation types relate, one must start by rewriting the BEP correlation in the same general form as the TSS correlation that estimates the transition state energy. This can be done easily by using the identities

$$\Delta\hat{H} = \hat{E}_{FS} - E_{IS} \tag{3}$$

and

$$E_A = E_{TS} - E_{IS} \tag{4}$$

Substituting these identities into eq 1, we get

$$\hat{E}_{TS} - E_{IS} = \alpha(E_{FS} - E_{IS}) + \beta \tag{5}$$

which can be rearranged to give

$$\hat{E}_{TS} = \alpha E_{FS} + (1 - \alpha)E_{IS} + \beta \tag{6}$$

We see here that estimating the activation energy and estimating the transition state energy are mathematically equivalent.

If we require that the initial and final state energies are invariant between the two correlation types and that the BEP and TSS correlations will, on average, give the same estimates (i.e., $\hat{E}_{TS}$ is the same for both correlations), then the mapping between the correlation types is immediately apparent. The slopes are related by

$$\alpha' = \alpha \tag{7}$$

whereas the intercepts are related by

$$\beta' = (1 - \alpha)E_{IS} + \beta \tag{8}$$

In the case of activated adsorption over a range of metals (as in Logadottir et al.[54] and similar works), because the initial state energy can be taken as zero for all points, the TSS and BEP correlations are equivalent. (Had the final state energy been approximated as a constant value rather than the initial state energy, a similar correlation in terms of the initial state energy but differing quantitatively in the constants would have been the result.) If we assume that the parameters will be obtained

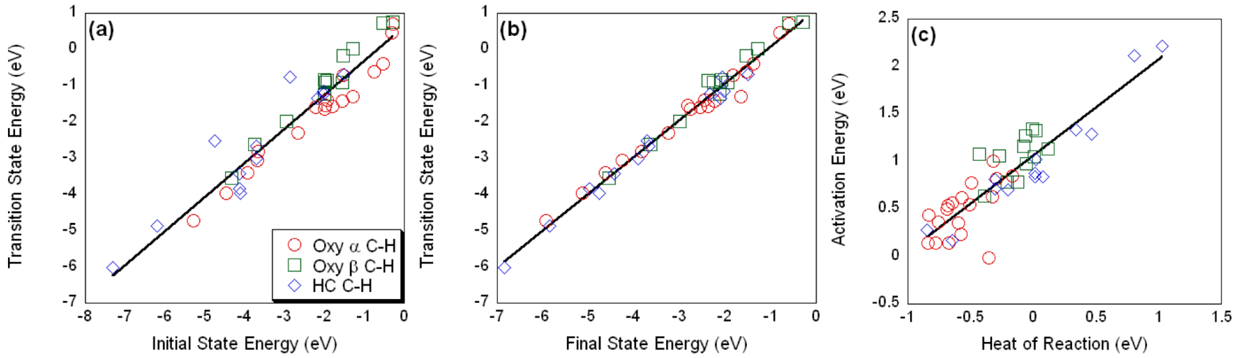

Figure 2. Examples of the reported correlation types applied to data from this work for C−H reactions in C_1 and C_2 mono-oxygenates and hydrocarbons. Panels a and b present the TSS correlation with the initial and final state as the independent variable, respectively. Panel c presents the BEP correlation. All reactions were written in the decomposition direction.

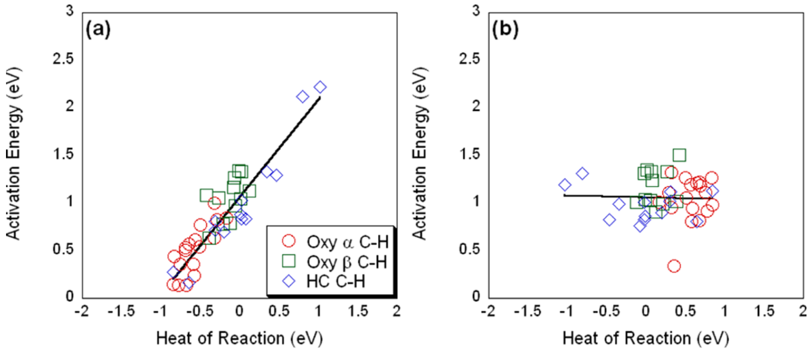

Figure 3. Illustration of the reversible nature of the BEP correlation with (de)hydrogenation reactions using C−H reaction data from this work. Panels a and b show the correlation when all reactions are written in the decomposition and synthesis directions, respectively.

via ordinary least-squares regression, then we can easily find their exact value. It is well-known from ordinary least-squares regression[62] that for a linear function with one independent variable,

$$Y = \alpha X + \beta \tag{9}$$

the slope can be calculated as

$$\alpha = \frac{\mathrm{Cov}[X, Y]}{\mathrm{Var}[X]} \tag{10}$$

and the intercept as

$$\beta = \overline{Y} - \alpha\overline{X} \tag{11}$$

where the overbars indicate a mean value. Thus, for the BEP correlation, we find

$$\alpha = \frac{\mathrm{Cov}[\Delta H, E_{\mathrm{A}}]}{\mathrm{Var}[\Delta H]} \tag{12}$$

and

$$\beta = \overline{E}_{\mathrm{A}} - \alpha\Delta\overline{H} \tag{13}$$

Likewise, for the TSS correlation, these values are

$$\alpha = \frac{\mathrm{Cov}[E_{\mathrm{FS}}, E_{\mathrm{TS}}]}{\mathrm{Var}[E_{\mathrm{FS}}]} \tag{14}$$

and

$$\beta' = (1 - \alpha)\overline{E}_{\mathrm{IS}} + \overline{E}_{\mathrm{A}} - \alpha\Delta\overline{H} \tag{15}$$

We see from the preceding derivation that the TSS coefficients are closely related to the BEP coefficients and that the actual values will be determined by the distribution of energies used in the regression. Although these coefficients may depend on the parent molecule and metal surface (see Introduction), for late transition metals, the variations should be relatively weak.[31,48] A complete investigation of these effects is beyond the scope of the current work. The slope α (or transfer coefficient) is generally considered to be a measure of the earliness or lateness of the transition state.[19] In the classic BEP formalism, it is constrained to fall between zero and unity. A near-zero value of α indicates an early (or initial state-like) transition state, whereas a near-unity value indicates a late (or final state-like) transition state. In the TSS correlation, neglecting the initial state energy forces the transfer coefficient to be near unity because of the high inherent collinearity between the final and transition state energies (see Figure 2). In both correlations, the intercept represents an average energy that may be thought of as a convenient reference point. In the case of the BEP correlation, this is an activation energy, whereas for the TSS correlation, it is a transition state energy.

In its classic form, the BEP correlation is a linear function of the difference between the initial and final state energies. It can also be recast as an explicit linear function of the initial and final state energies with the transition state energy as the dependent variable. In contrast, the TSS correlation for estimating the transition state energy is a linear function of either the initial or final state energy alone (as chosen by the user), with the other approximated by a constant and included in the intercept. Thus, when the correlations are put in the appropriate functional forms, it is found that the TSS correlation is an approximation and simplication of the BEP correlation (most readily seen in the constant term). The BEP correlation is therefore general and should be applicable wherever the TSS correlation is applicable. We demonstrate this by examining a seeming contradiction in the literature.

Loffreda et al.[49] have suggested the BEP correlation is incapable of estimating activation energies of hydrogenation reactions and proposed the use of a TSS type correlation, instead. These workers found that there was a poor correlation between the heat of reaction and the activation energy for reactions written in the synthesis direction. However, recent work by Wang et al.[31] for dehydrogenation reactions has suggested that the BEP correlation may be preferable to the TSS correlation. In particular, they believe that trends in activation energies are more readily identifiable when using BEP correlations than when using TSS correlations. They also suggest that BEP correlations are more flexible than TSS correlations because they allow for the transfer coefficient to take on a wider range of values. Their conclusions in this regard are consistent with our conclusions. At first glance, the two papers seem to reach contradictory conclusions. This is not the case, however, and their results are easily reconciled.

As shown previously, both the BEP and TSS correlations can be cast in terms of the initial, final, and transition state energies. Loffreda et al.[49] rightly concluded that there was no correlation between the activation energy and heat of reaction when the reaction was written in the synthesis direction. In the context of our earlier derivation, this implies that the transfer coefficient α for dehydrogenation is close to unity and the transition state is late (or product like), as it is in Wang et al.[31] For hydrogenation, the quantity $1 - \alpha$ will be close to zero, implying that there is little or no correlation between the activation energy for hydrogenation and the heat of hydrogenation, consistent with the observation of Loffreda et al. This is clearly illustrated in Figure 3 for (de)hydrogenation reactions. When the reactions are written in the dehydrogenation direction, there is an excellent correlation. However, when they are written in the hydrogenation direction, little or no correlation is observed.

We wish to emphasize the inherent reversibility and flexibility of the BEP correlation. When written in a bivariate linear form analogous to the univariate linear TSS correlation, it is obvious that the two slopes are constrained to sum to unity. If a BEP slope is near zero (implying little correlation) for a set of reactions written in one direction, then the BEP formulation constrains the slope for the opposite direction to be near unity (implying high correlation). In both cases, the estimated transition state energies will be identical, and in the event that a set of reactions has an intermediate transition state (i.e., a transfer coefficient near 0.5), the BEP correlation will correctly estimate that slope, as well, with a correspondingly lower degree of correlation. The important conclusion here is that no matter which direction the reactions are written in, as long as they are written consistently, the BEP correlation will give the best estimate achievable with a simple linear correlation.

We next turn our attention to the effect of the reference state on the value of the correlation parameters. We do this by subtracting a common, arbitrary reference energy E_{ref} from each of the initial, transition, and final state energies in eq 6. This gives

$$\hat{E}_{\mathrm{TS}} - E_{\mathrm{ref}} = \alpha(E_{\mathrm{FS}} - E_{\mathrm{ref}}) + (1 - \alpha)(E_{\mathrm{IS}} - E_{\mathrm{ref}}) + \beta \qquad (16)$$

If we then rearrange this into the traditional BEP form, it is trivial to see that the reference energy will have no effect on the correlation parameters because the reference energy terms will subtract out. However, if we are concerned with the TSS correlation (i.e., holding the initial state energy constant), this is not the case. The reference energy will affect the values of both the slope and intercept. The new values are

$$\alpha = \frac{\mathrm{Cov}[(E_{\mathrm{FS}} - E_{\mathrm{ref}}), (E_{\mathrm{TS}} - E_{\mathrm{ref}})]}{\mathrm{Var}[(E_{\mathrm{FS}} - E_{\mathrm{ref}})]} \qquad (17)$$

and

$$\beta' = (1 - \alpha)(\bar{E}_{\mathrm{IS}} - \bar{E}_{\mathrm{ref}}) + \bar{E}_{\mathrm{A}} - \alpha\Delta\bar{H} \qquad (18)$$

The numerical impact of the choice of some possible reference states will be explored later. For now, it is sufficient to note that the TSS correlations are actually a family of related correlations.

4. IDENTIFICATION OF A HOMOLOGOUS SERIES

For identification of homologous series, we include results from methane, ethane, methanol, and ethanol on Pt(111). For each molecule and fragment, we considered C−H, O−H, C−C, and C−O as possible reaction types. The addition of O to methane and ethane to one of the reactive C centers to form methanol and ethanol may alter the chemical structure of the C−H and C−C bonds. We therefore subdivided the C−H and C−C reactions on the basis of the available reactive C centers for each molecule. In the case of ethanol, the α C and β C positions were considered to be unique and distinguishible. For deoxygenation reactions, because of differences in the strength of adsorption as well as chemical differences in the oxygen-containing species produced (i.e., OH and O), we distinguished hydroxyl-terminated species from carbonyl-/alkoxide-terminated species. Preliminary testing showed that (1) methane and ethane could be grouped together for C−H reactions and (2) methanol and ethanol could be grouped together for the α C−H, C−O, and C−OH reaction types. Overall, we considered three types of C−H reactions (α C−H and β C−H in oxygenates and C−H in hydrocarbons), a single type of O−H reaction in alcohols, two types of C−C reactions (C−C in oxygenates and C−C in hydrocarbons), and two types of C−O reactions (OH and O terminated).

Given the inherent chemical similarity of some of the reactions, further work was carried out to test whether certain subgroups of reactions could be grouped together to reduce the total number of correlations. Specifically, we considered the C−H, C−C, and C−O reaction subtypes for possible grouping into combined C−H, combined C−C, and combined C−O correlations. Since there is only one type of O−H reaction and it is not expected to be chemically similar to any of the other reaction types, we do not consider O−H reactions in the treatment that follows.

For two correlations to be statistically the same, they must meet two simple criteria: equality of slopes and equality of intercepts. Aside from outliers and high leverage points (i.e., a point whose presence or absence has a large effect on the slope), the slope is independent of the sampled reaction energetics. On the other hand, the intercept is very sensitive to the sampled reaction energetics. Systematically high (low) values of the independent and dependent variables will lead to higher (lower) values of the intercept. Although the two intercepts will apparently differ quantitatively, because the width of the confidence interval is a function of the mean value of the independent variable (see the Supporting Information), they will still be statistically equal.

To simplify the comparison of seemingly different but statistically equal values, we choose to shift or recenter all data to a common reference point. For convenience, this reference point is where the mean value of the recentered independent variable is zero and is simply accomplished by subtracting the mean value of the independent variable from both the independent and dependent variables. The BEP correlation was shown earlier to be a better choice in general than the TSS correlations. Furthermore, the larger variances inherent to the final and transition state energies result in intercept confidence intervals so large as to make different homologous series statistically indistinguishable (see the complete tables in the Supporting Information). As such, we focus our attention on the BEP correlation. If we start with eq 1, subtract the mean value of the heat of reaction from both sides and make appropriate substitutions for the intercept β, we get the following equation:

$$E_{\mathrm{A,f}} - \Delta\bar{H} = \alpha(\Delta H - \Delta\bar{H}) + \bar{E}_{\mathrm{A,r}} \qquad (19)$$

This equation indicates that the intercept for the recentered correlation is simply the mean value of the reverse activation energy. The parameters for the shifted correlations are given in Table 3.

As a standard statistical test of equality, we will simply compare the interval estimates for the slopes and intercepts. If the intervals overlap, then the parameters are judged to be equal. In comparing the parameters, we find that only the C−OH and C−O correlations are statistically different. We note also that the slopes are not a reliable means of differentiating homologous series on a single metal surface. All slopes in Table 3 are statistically equal. This is due in part to the inherent lateness of the decomposition reactions on late transition

Table 3. Slopes and Intercepts with 95% Confidence Intervals for the Recentered Correlations of Selected Homologous Series in C_1 and C_2 Hydrocarbons and Mono-Oxygenates

correlation	no. points	α	$\bar{E}_{A,r}$ (eV)
oxygenate α C−H	18	0.80 ± 0.61	1.04 ± 0.14
oxygenate β C−H	12	0.73 ± 0.78	1.17 ± 0.14
hydrocarbon C−H	13	1.10 ± 0.20	0.98 ± 0.12
oxygenate C−C	24	0.62 ± 0.43	1.66 ± 0.21
hydrocarbon C−C	9	0.68 ± 0.14	1.69 ± 0.32
C−OH	16	0.69 ± 0.33	1.17 ± 0.28
C−O	16	0.84 ± 0.17	1.78 ± 0.20

metals as noted by Wang et al.[31,48] Further, the small sample size and considerable scatter in some of the DFT results (e.g., for oxygenate β C−H reactions) can result in large confidence intervals for the slopes. The resulting homologous series are therefore combined C−H, O−H, combined C−C, C−OH, and C−O as judged on the basis of chemical similarity and statistically different correlation parameters. The final correlations are shown in Figure 4, and the parameters are given in Table 4.

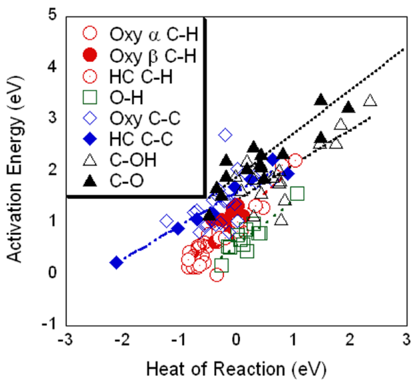

Figure 4. BEP correlations for homologous series identified using recentered DFT data. Identified correlations are C−H, O−H, C−C, C−OH, and C−O. Only the trend lines for the final correlations are shown; parameters are given in Table 4.

Table 4. BEP Correlation Parameter Values and 95% Confidence Intervals for Final Homologous Series

correlation	no. points	α	β (eV)
combined C−H	43	1.02 ± 0.16	1.06 ± 0.08
O−H	13	0.86 ± 0.28	0.56 ± 0.11
combined C−C	33	0.66 ± 0.21	1.59 ± 0.13
C−OH	16	0.69 ± 0.33	1.43 ± 0.35
C−O	16	0.84 ± 0.17	1.87 ± 0.19

5. DEVIATION CHARACTERISTICS OF THE TSS AND BEP CORRELATIONS

Both the BEP and TSS correlations are ultimately used for estimating activation energies, and deviations in the estimates can have a significant effect on model results. What is fundamentally more important than good correlation fits (e.g., high R^2 values) is good estimates of activation energies or transition state energies. Therefore, we further investigated the behavior of the BEP and TSS correlations by deriving expressions for the deviations between the BEP estimates and the DFT results.

If we once again assume that the correlation parameters are obtained via ordinary least-squares regression, we can easily develop expressions for the deviation. For this case, it is well-known that the deviation is given by

$$\varepsilon = Y - \hat{Y} \tag{20}$$

where Y is the actual value of the dependent variable and $\hat{Y}$ is its estimate. It is trivial to show that for both the BEP and TSS correlations,

$$\varepsilon = E_{\mathrm{TS}} - \hat{E}_{\mathrm{TS}} \tag{21}$$

which further highlights the equivalence of estimating the activation energy and the transition state energy. The mean deviation in both cases is identically zero, implying that the correlations are unbiased estimators. The variance for the deviations in a linear correlation is

$$\mathrm{Var}[\varepsilon] = \mathrm{Var}[Y] + \mathrm{Var}[\hat{Y}] - 2\mathrm{Cov}[Y, \hat{Y}] \tag{22}$$

Applying these expressions to the BEP and TSS correlations, we find that the variance for these correlations is

$$\mathrm{Var}[\varepsilon] = \mathrm{Var}[E_{\mathrm{TS}}] + \mathrm{Var}[\hat{E}_{\mathrm{TS}}] - 2\mathrm{Cov}[E_{\mathrm{TS}}, \hat{E}_{\mathrm{TS}}] \tag{23}$$

If Cov[Y,$\hat{Y}$] ≈ Var[Y] ≈ Var[$\hat{Y}$] (a good assumption for highly correlated quantities), then the total variance in the deviations will be about an order of magnitude less than the magnitude of the individual terms. Because the BEP correlation adds an additional fitting variable, it will typically give better fits (i.e., smaller deviations from the DFT results) to activation (or transition state) energies. This is illustrated quantitatively below.

All three possible correlation types (i.e., initial state TSS, final state TSS, and BEP) were tested to investigate the variances in the raw deviation. For the TSS correlations, the reference state was taken to be the DFT energy of the gas phase form of the adsorbate as this reference state gave the best estimates for the correlation parameters, and the deviation statistics for all tested reference states were very similar. The correlation parameters used are included in the Supporting Information. The tested homologous series were the combined C−H, O−H, combined C−C, C−OH, and C−O correlations. Deviations between the DFT value and the correlation estimate were calculated as

$$\varepsilon = E_{\mathrm{DFT}} - E_{\mathrm{correlation}} \tag{24}$$

The resulting distributions are presented in Figure 5. All distributions are approximately symmetric with relatively few outliers. It is clear from this figure that the initial state TSS correlations give the widest variation. The final state TSS and the BEP correlations are roughly equivalent, but overall, the BEP correlation appears to be slightly better, consistent with the preceding discussion.

6. COMPUTATIONAL EFFECTS

The last topic considered is the effect of the DFT calculations and postprocessing of the DFT results (via different choices of reference energy) on the correlation parmeters. We will first investigate the effect of different reference states on the TSS correlation parameters. Then we will specifically examine the effect of unit cell size (with ethanol), the zero point energy correction (with ethylene glycol), and the effect of the parent molecule on the correlation by comparing results for ethanol

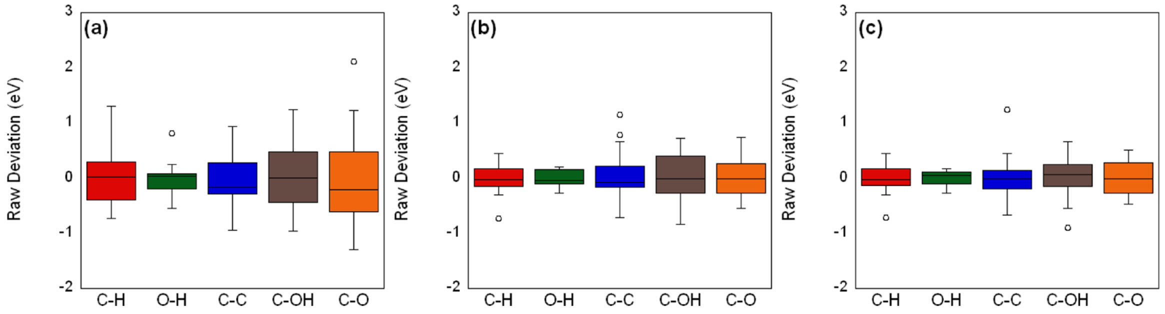

Figure 5. Box plots of the distributions of the raw deviations in the correlations for ethanol decomposition. Panels are for (a) initial state TSS, (b) final state TSS, and (c) BEP correlations. The deviation is defined to be the difference between the DFT value and the correlation estimated value. A positive/negative deviation indicates the correlation estimate is too low/high. Overall, the traditional BEP correlation appears to give the best results.

Table 5. Effect of the Reference Energy on Theoretically Calculated and Regressed (with 95% Confidence Intervals) TSS Correlation Parameters

		total energies		heats of formation		binding energies	
series	parameter	theory	regression	theory	regression	theory	regression
combined C−H	α	1.00	1.00 ± 0.00	1.00	1.00 ± 0.00	1.01	1.01 ± 0.04
	β' (eV)	−2.63	−2.63 ± 3.22	0.87	0.87 ± 0.18	1.09	1.08 ± 0.13
O−H	α	1.00	1.00 ± 0.00	1.00	1.00 ± 0.00	1.00	1.00 ± 0.06
	β' (eV)	6.33	6.33 ± 15.93	0.90	0.90 ± 1.01	0.53	0.53 ± 0.19
combined C−C	α	1.00	1.00 ± 0.00	1.00	1.00 ± 0.00	1.03	1.03 ± 0.08
	β' (eV)	1.88	1.88 ± 8.74	1.68	1.68 ± 0.51	1.77	1.76 ± 0.32
C−OH	α	1.00	1.00 ± 0.00	1.00	1.00 ± 0.00	1.10	1.10 ± 0.16
	β' (eV)	4.54	4.54 ± 39.77	1.38	1.38 ± 2.48	1.33	1.41 ± 0.47
C−O	α	1.00	1.00 ± 0.00	1.00	1.00 ± 0.00	1.03	1.03 ± 0.13
	β' (eV)	9.64	9.64 ± 28.57	2.26	2.26 ± 1.75	1.83	1.85 ± 0.33

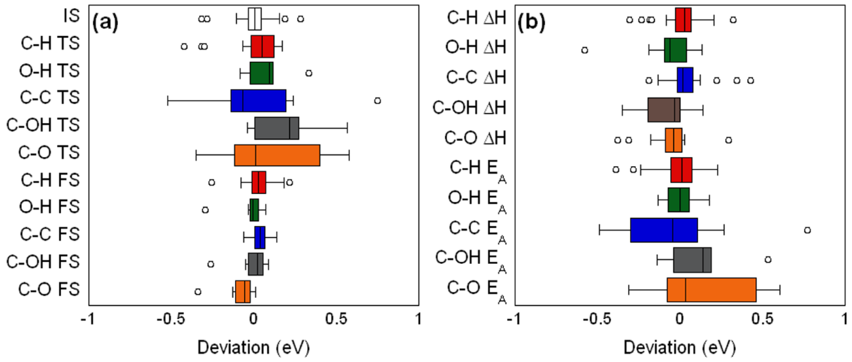

Figure 6. Distribution of deviations in absolute and relative (reaction) energies in ethanol on 2 × 2 and 3 × 3 unit cells. Panel a/b shows the deviations in the binding energies/heat of reaction and activation energies. The deviation is defined with respect to the 2 × 2 unit cell. There do not seem to be significant effects on the binding energies of the stable adsorbates, possibly because the final (decomposed) states were taken with a separate slab reference state in which interactions are neglected. The transition state and activation energies of the C−C, C−OH, and C−O reactions show significant deviations.

and ethylene glycol (both on 3 × 3 unit cells and without the zero point energy correction).

There are many possible choices for reference energies, and a full investigation of every possible choice is beyond the scope of this work. Nevertheless, there are two basic categories of reference energy that will illustrate the principles involved. The first type is a constant common to all points (e.g., the total energy of the pure slab), and the second type depends on the adsorbate (e.g., referencing each adsorbate to its corresponding gas phase form). The first case corresponds to surface heats of formation, whereas the latter corresponds to the typical binding energies reported in the literature. We will investigate both here and compare them to correlation parameters obtained from the raw DFT output.

Starting with eqs 17 and 18, we can determine the effect of the two postulated reference energies. In the first case, because the reference energy is a constant, it can be shown that

$$\alpha = \frac{\mathrm{Cov}[(E_{\mathrm{FS}} - E_{\mathrm{ref}}), (E_{\mathrm{TS}} - E_{\mathrm{ref}})]}{\mathrm{Var}[(E_{\mathrm{FS}} - E_{\mathrm{ref}})]} = \frac{\mathrm{Cov}[E_{\mathrm{FS}}, E_{\mathrm{TS}}]}{\mathrm{Var}[E_{\mathrm{FS}}]} \tag{25}$$

That is, the slope is unaffected by the choice of the reference energy. In the second case, because the reference energy is itself a variable, the slope will be affected. In both cases, the intercept

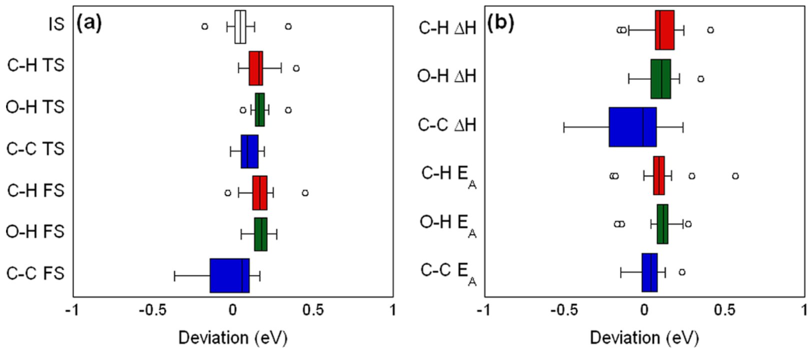

Figure 7. Distribution of deviations in absolute and relative (reaction) energies in ethylene glycol on 3 × 3 unit cells with and without the zero point energy correction. Panel a/b shows the deviations in the binding energies/heats of reaction and activation energies. The deviation is defined with respect to the uncorrected energies and is thus equal to the negative of the zero point energy correction. The zero point energy correction systematically reduces the binding energies, heats of reaction, and activation energies for the hydrogenation reactions, whereas energies for the C−C reactions are not affected as much. In the reported data,[60] it was assumed that C−O reactions in ethylene glycol on Pt(111) were unimportant.

is affected by the choice of the reference energy. The numerical results demonstrating this are given in Table 5.

We find that agreement between the theoretical and regressed values is excellent in every case. Further, we find that the quality of the estimated intercept (as measured by the size of the 95% confidence intervals) is best when the binding energy reference is used. This is likely due to the fact that the total energies are of order 10^4 eV, the heats of formation are of order 10^3 eV, and the binding energies are of order 1 eV (see Supporting Information). Since the activation energies are themselves order 1 eV, the use of total energies or heats of formation (note that both are highly dependent on the DFT code used) results in independent and dependent variables that are badly scaled for the regression. Overall, we find that the highest quality regressions are obtained when the independent and dependent variables are of approximately the same order of magnitude as the heat of reaction and the activation energy. As noted previously, the reference state chosen does not appear to have a large effect on the quality of the estimated transition state energies.

The effects of cell size and zero point energy are investigated principally by calculating the difference between corresponding values relative to 2 × 2 unit cells (Figure 6) and without the zero point energy correction (Figure 7), respectively. We present in these figures the deviations in the binding energies, heats of reaction, and activation energies.

The mean deviations from Figure 6 suggest that C−H, O−H, and C−C reactions are relatively insensitive to coverage effects. The C−OH and C−O reactions, on the other hand, are somewhat sensitive. The mean deviations are small enough, however, that the parameters for correlations derived from calculations performed on 3 × 3 cells are not likely statistically different from the corresponding parameters estimated using calculations from 2 × 2 cells. This is readily seen in Table 6. Further, the mean deviations are all well within the inherent accuracy of the DFT calculations (this is typically around 0.25 eV). Taken together, coverage effects may have a strong effect on the energetics of individual reactions, but they do not have a significant impact on the correlation parameters. This is illustrated by the values in Table 6. The C−O BEP correlation has the largest change in intercept, but even this is within the confidence intervals. We also checked whether the deviations in the heats of reaction and the activation energies were significantly correlated and found that they were not.

Table 6. Comparison of Ethanol BEP Parameters with 95% Confidence Intervals for Reactions As a Function of Unit Cell Size

correlation	no. points	cell size	α	β (eV)
α C−H	12	2 × 2	0.72 ± 0.79	0.90 ± 0.48
		3 × 3	0.58 ± 0.77	0.82 ± 0.47
β C−H	12	2 × 2	0.73 ± 0.78	1.14 ± 0.16
		3 × 3	0.58 ± 0.86	1.17 ± 0.20
O−H	7	2 × 2	0.78 ± 0.67	0.56 ± 0.17
		3 × 3	1.10 ± 0.54	0.43 ± 0.16
C−C	15	2 × 2	1.10 ± 0.83	1.81 ± 0.30
		3 × 3	0.87 ± 0.59	1.77 ± 0.20
C−OH	6	2 × 2	0.50 ± 1.08	1.38 ± 0.96
		3 × 3	0.24 ± 0.73	1.42 ± 0.67
C−O	7	2 × 2	0.62 ± 0.36	1.94 ± 0.29
		3 × 3	0.87 ± 0.43	1.69 ± 0.35

Figure 7 shows clear systematic deviations due to the zero point energy correction. We present the correlation parameters for the two cases in Table 7. In all cases, there does not appear to be a statistical difference in the correlations, although it is interesting that the intercepts for the zero point energy corrected correlations are systematically lower.

Table 7. Comparison of BEP parameters with 95% confidence intervals for ethylene glycol reactions as a function of zero point energy correction

correlation	no. points	ZPE	α	β (eV)
C−H	24	no	0.54 ± 0.59	0.74 ± 0.26
		yes	0.36 ± 0.62	0.62 ± 0.32
O−H	18	no	0.72 ± 0.28	0.43 ± 0.12
		yes	0.83 ± 0.24	0.38 ± 0.08
C−C	20	no	1.11 ± 0.57	1.80 ± 0.39
		yes	0.65 ± 0.49	1.43 ± 0.33

As with the cell size deviations, we checked for correlations between the heats of reaction and the activation energies. Interestingly, we found that there were statistically significant correlations for all three types of reactions. The correlations follow the relationship

$$\Delta_{\mathrm{ZPE}}E_{\mathrm{A}} = \alpha\Delta_{\mathrm{ZPE}}(\Delta H) + \beta \tag{26}$$

That is, the change in the activation energy due to the zero point energy correction in the initial and transition states is linearly correlated with the change in the heat of reaction due to the zero point energy correction in the initial and final states. We will refer to this correlation as the zero point energy correlation.

The correlation parameters are given in Table 8. In all cases, the constant is very close to zero, implying that little or no portion of the inherent barrier is due to the zero point energy correction. Although all slopes are statistically the same, the slopes for the two dehydrogenation reaction types are nearly identical, but the C−C reaction correlation has a lower slope. What this suggests (and is consistent with Figure 7) is that the zero point energy correction has a more significant effect on the activation energies for the dehydrogenation reactions than for the C−C cracking reactions. Because the zero point energy is a linear function of the vibrational frequencies, which are, in turn, a function of the atomic masses, we suggest that one reason the slopes for the dehydrogenation reactions are so similar is the similarity of the differences in the atomic masses involved. This would also explain why the slope for the C−C reaction is lower and would also suggest that the slope for a zero point energy correlation for C−O cracking reactions should be similar to the C−C correlation. Finally, we suggest that the zero point energy correlations may be useful for estimating zero-point-energy-corrected activation energies using the nonzero-point-energy-corrected BEP correlations, which are frequently found in the literature.

Table 8. Correlations Parameters with 95% Confidence Intervals Relating the Change in Heat of Reaction and Activation Energy Due to the Zero Point Energy Correction for Ethylene Glycol

correlation	no. points	α	β (eV)
C−H	24	0.73 ± 0.40	−0.02 ± 0.06
O−H	18	0.72 ± 0.38	−0.03 ± 0.06
C−C	20	0.28 ± 0.16	−0.06 ± 0.03

To illustrate the potential utility of such an approach, we compared the estimates produced via three different methods to the actual DFT zero point energy corrected activation energies: (1) zero-point-energy-corrected heats of reaction in the nonzero-point-energy-corrected BEP correlation, (2) nonzero-point-energy-corrected heats of reaction with the nonzero-point-energy-corrected BEP correlation and then corrected with the zero point energy correlation, and (3) zero-point-energy-corrected heats of reaction with the zero-point-energy-corrected BEP correlation. The box plots comparing the deviations are given in Figure 8. We find that methods 2 and 3 give very similar results and that little additional error is introduced by using method 2 for a lower computational cost.

Although we cannot rigorously address the effect of the parent molecule on the correlations with the limited amount of data on hand, we can make some suggestions by comparing the ethanol and ethylene glycol correlations derived from the calculation sets performed for 3 × 3 unit cells without the zero point energy correction. The correlation parameters in Table 9 suggest that the correlation parameters for corresponding reaction types of ethanol and ethylene glycol are statistically the same. Finally, it has also been reported by Laref et al.[64] that initial state TSS correlations for the hydrogenation of acrolein are also applicable to crotonaldehyde and prenal. Their results for initial state TSS correlations should carry over to BEP correlations. Although not exhaustive, this brief comparison does suggest that BEP correlations will be applicable to molecules beyond the training set.

Table 9. Comparison of BEP Parameters with 95% Confidence Intervals for Reactions As a Function of Parent Molecule

correlation	no. points	α	β (eV)
ethanol α C−H	12	0.58 ± 0.77	0.82 ± 0.47
ethylene glycol C−H	24	0.54 ± 0.59	0.74 ± 0.26
ethanol O−H	7	1.10 ± 0.54	0.43 ± 0.16
ethylene glycol O−H	18	0.72 ± 0.28	0.43 ± 0.12
ethanol C−C	15	0.87 ± 0.59	1.77 ± 0.20
ethylene glycol C−C	20	1.11 ± 0.57	1.80 ± 0.39

7. CONCLUSIONS

Although intensive work has been devoted to developing correlations of energetics of surface reactions for the past 10 years using DFT, there has been limited understanding of their range of applicability and their relative error in predicting activation energies. Lumping of reactions in fewer groups (homologous series) has been the dominant trend to minimize the number of DFT calculations. Published calculations are performed with different DFT codes and numerical parameters,

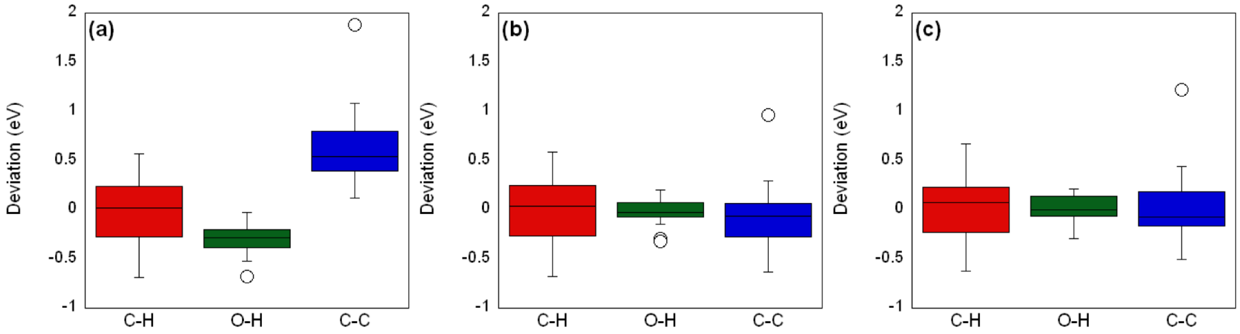

Figure 8. Comparison of deviations in correlations accounting for the zero point energy correction. Panel a shows the case in which zero-point-energy-corrected heats of reaction were used with the nonzero-point-energy-corrected correlation. Panel b shows the case in which the nonzero-point-energy-corrected values are used with the nonzero-point-energy-corrected correlation and then corrected with the zero point energy correlation. Panel c shows the case in which the zero-point-energy-corrected heats of reaction are used with the zero-point-energy-corrected correlation. Overall, both panels b and c show similar results.

making meaningful statistical comparison impossible. In this paper, we have addressed four principal topics: (1) how the transition state scaling and Brønsted−Evans−Polanyi correlation types are related theoretically, (2) how to determine the independence of proposed homologous series, (3) the error of the correlations, and (4) what effects computational rigor/level of theory and the identity of the parent molecule have on the correlation parameters. To address these points, many DFT calculations were performed with the same DFT code and numerical parameters.

We found that the BEP correlation is a linear function of both the initial and final state energies with the transfer coefficient α appearing in both terms. In the final state term, the slope is α, and in the initial state term, the slope is $1 - \alpha$. The intercept is a simple weighted average of the average forward and reverse activation energies. The initial (final) state TSS correlation is an approximation of the BEP correlation derived by making the further assumption that the final (initial) state energy is constant and incorporating it into the intercept.

We also developed a protocol for determining when homologous series can be lumped together. Two correlations are equivalent if their parameters are statistically equal as determined by the parameters' confidence intervals. We then applied this protocol to a number of reaction types found in ethanol thermal decomposition: α C−H, β C−H, hydrocarbon C−H, O−H, oxygenate C−C, hydrocarbon C−C, C−OH, and C−O reactions. We found that all C−H reactions may be grouped as a single C−H series. Likewise, we found that all C−C reactions form a single series. Interestingly, we found that this is not the case for C−O reactions: C−OH and C−O reaction types were different.

By developing a theoretical expression (in the Supporting Information) for the variance in the deviations between the DFT and correlation estimates, we found that the BEP correlation with an extra fitting variable has a smaller variance in the deviation than the TSS correlations. This implies that the BEP correlation gives better fits to activation energies with smaller deviations, on average, than the TSS correlations. This theoretical result was confirmed numerically by calculating the deviations between actual DFT results and the corresponding correlation estimates. This is the first time that a statistical comparison of the different types of correlations has been conducted with respect to the deviations in the activation energies and transition state energies of chemical reactions. Our results clearly show that the BEP correlation should be preferred.

Finally, we investigated the effects of the reference state, the unit cell size, the zero point energy correction, and the parent molecule on the resulting correlation parameters. We found that the reference state has the most effect on the intercepts but little effect on the quality of the estimated activation energies. We also found that although cell size effects are important for certain individual reactions, there is little effect on the average values of the initial, final, and transition state binding energies, the heats of reaction, and the activation energies. Thus, cell size affects the correlation parameters only slightly. The zero point energy correction, however, has a systematic effect on the average values of the binding energies, heats of reaction, and activation energies. Interestingly, we found that it was possible to correlate the change in activation energy due to the zero point energy correction with the corresponding change in the heat of reaction for C−H, O−H, and C−C reactions of ethylene glycol. Applying this corrective correlation to the nonzero-point-energy-corrected BEP correlation yielded results similar to the case in which the fully zero-point-energy-corrected correlation was used. In all cases, the zero point energy correction is most important for (de)hydrogenation reactions. We also showed that analogous reactions for ethanol and ethylene glycol thermal decomposition fall on the same correlations. This indicates that BEP correlations may be useful for parent molecules other than the one(s) for which they were initially developed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information contains the complete set of energies used in the regressions, the definitions used in calculating the 95% confidence intervals, a brief discussion of box plots and their interpretation, an alternate derivation of the expressions for the variance of the deviations for the BEP and TSS correlations, and tables with correlation parameters for all possible BEP and TSS correlations for the ethanol and ethylene glycol data used in this work. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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