Reply to Comment on “Identity Hydrogen Abstraction Reactions, $X^\bullet + H{-}X' \rightarrow X{-}H + X'^\bullet$ ($X = X' = CH_3, SiH_3, GeH_3, SnH_3, PbH_3$): A Valence Bond Modeling”

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Zavitsas criticized the title paper[1] on the grounds that (a) it inaccurately emphasizes the importance of the “polar” effect, (b) its BOVB calculated barriers are far from experimental values; and (c) its VB model is deficient because it allegedly lacks an important structure. The author of the comment further points out that his own model,[2] for hydrogen abstraction, is far more accurate, than the VB model, and advocates its use. In our reply we first respond to the criticism. Subsequently, by delineating the relationship between the VB model and that of Zavitsas (Z), we show that the Z-model: (i) is based on an incomplete theory, and as such it leads to a wrong mechanism of activation and (ii) that it works due to fortuitous cancellation of errors. Scheme 1 includes a few drawings required for the discussion of the identity hydrogen transfer reaction, eq 1:

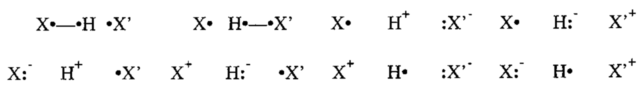
$$X^\bullet + H{-}X' \rightarrow X{-}H + X'^\bullet \qquad (1)$$

The Polar Effect. Zavitsas rightly argues that Hammett correlations, used by the community of physical organic chemists, do not actually prove the importance of ionic structures in the transition state (TS) of hydrogen abstraction reactions. However, he goes a step further and questions generally the contribution of ionic structures to the TS. Our VB study clearly shows[1] (Table 1 there) that the ionic structures, Scheme 1a, contribute more heavily to the TS than to the reactant state. Mere inspection of the calculated (CCSD(T)/6-31G*) charges on the transferred hydrogen atom, Q_H, in the TS reveals precisely the same trend, e.g., for $X = CH_3$ the charge is $Q_H = +0.11$, and for $X = F$ it is $Q_H = +0.485$. Thus, the ionic structures are quite prominent. However, as argued,[1] their specific influence in this set of identity reactions is masked in the sense that they do not perturb the regular trends set by the other reactivity factors. Even if objections to the “polar effect” have been raised (see references in the comment), it is still a widely used concept in radical chemistry.[3−5]

BOVB Barriers. Zavitsas argues that BOVB, which is an ab initio method, exhibits a major shortcoming, because the calculated barriers deviate considerably from the experimental activation energies (E_a). The BOVB calculations were aimed[1] at reproducing the classical barriers and trends obtained by ab initio methods such as CCSD(T). It is well-known that ab initio calculations, unless they use a very large basis set and a high-level electron correlation treatment, generally overestimate barriers.[6] It is unreasonable, therefore, to expect that our BOVB calculations would be better than CCSD(T) barriers. In fact, it is an achievement of the BOVB method to perform as well as it does, *with only eight VB structures*.

SCHEME 1

(a) VB structures for reaction (1):



(b) Structures for reaction (1) used by Zavitsas:

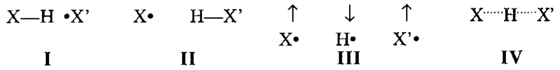


TABLE 1: Repulsion Energies[a] in X−H−X′ TS’s

X	H	CH_3	SiH_3	GeH_3	SnH_3	PbH_3	F	Cl	Br
$^3E_{XX'}{}^‡$	9.5	17.8	14.0	11.3	10.6	8.6	5.6	8.1	8.1
$^3E_{HX'}{}^‡$	97.1	106.3	83.7	77.9	68.3	62.9	127.0	96.5	83.1

[a] In kcal/mol. Calculated by use of the VB method described in ref 1.

The ab initio-experiment discrepancy is yet another problem which is, of course, extremely important but beyond the scope of our work.[6b] Having said that, it is still important to stress that the trends in the computed barriers for reaction 1 are the same at all the levels used in our study,[1] and therefore we are quite confident that when experimental quantities will become available, they will reflect the same trend, namely *that the barrier decreases down the column, in the order* $X = CH_3 > SiH_3 > GeH_3 > SnH_3 > PbH_3$. In this respect, the reader is encouraged to consult the exchange between Roberts and Zavitsas regarding the barriers for $X = CH_3$ and SiH_3.[7] Also relevant is the conclusion of Dubey et al.,[8] that computed barriers for a variety of hydrogen abstraction reactions correlate with E_a values.

The Z-Model vis-à-vis the VB Model: Which One Is Actually Right? Zavitsas questions the validity of the VB model because the structure set used in ref 1 (shown in Scheme 1a here) allegedly lacks an important structure, labeled as **III** in Scheme 1b. The spin-alternate structure, **III**, suffers triplet repulsion (Pauli repulsion) between its end groups in the X- -H- -X′ TS, and this repulsive energy, $^3E_{XX'}$ is the major cause of the barrier in the Z-model,[10,11] as well as in the related BEBO model.[12] It should be clear, at the outset, that the VB structure set in Scheme 1a is a complete valence set for reaction 1, in which three valence electrons participate in the reorganization of the bonds.[9] Since this valence set is complete, the question then becomes: what kind of structure is **III** that figures so prominently in Zavitsas modeling (Z-model) of reaction 1?

The structure set used to model the TS in the Z-model is shown in **I**−**IV** in Scheme 1b.[10] Structures **I** and **II** are the well-known canonical Lewis structures in the VB model (a Lewis structure is a mixture of a covalent and two ionic structures, in Scheme 1a). **III**, however, is not a proper structure, but rather a single determinant with an indefinite spin (it is just an eigenfunction of the $\mathbf{S}_z$ operator but not of $\mathbf{S}^2$).[13] Moreover, **III**

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is redundant since it is part of the wave functions of both structures **I** and **II**, as can be easily seen by writing these wave functions.[14] Structure **IV** cannot stand on its own and is simply the linear combination **I** + **II**.[1,14,15] The use of improper structures to determine the energy of the TS leads to a fundamental flaw in the Z-model, as discussed below.

Both the VB and the Z-model locate the TS at the geometry where the Lewis structures have equal energy, i.e., $E_{\mathbf{I}} = E_{\mathbf{II}}$. In both models, this is the crossing points (E_c) of the canonical structures of reactants and products. In both models, the barrier is expressed by eq 2, as a balance between the height of this crossing point, ΔE_c, and the resonance energy (B) gained by delocalizing the three electrons over the three centers in X- -H- -X′. The height of the crossing point is expressed in eq 3, using labels of the Z-model,[10.11] as the energy difference of structure **I** at the TS ($E_I^{\ddagger}$) and at the reactant state (E_I^{0}). The resonance energy B corresponds to negative value of the quantity in the Z-model, as expressed in eq 4.

$$\Delta E^{\ddagger} = \Delta E_c - B \tag{2}$$

$$\Delta E_c = E_I^{\ddagger} - E_I^{0} \tag{3}$$

$$B = -E_R^{\ddagger} \tag{4}$$

Using VB theory, the correct quantum mechanical expression for $E_I^{\ddagger}$ is given by eq 5a, while the ΔE_c is given by eq 5b

$$E_I^{\ddagger}(\mathrm{VB}) = {}^1E_{XH}^{\ddagger} + 0.5[{}^3E_{XX'}^{\ddagger} + {}^3E_{HX'}^{\ddagger}] \tag{5a}$$

$$\begin{aligned}\Delta E_c(\mathrm{VB}) &= {}^1E_{XH}^{\ddagger} - {}^1E_{XH}^{0} + 0.5[{}^3E_{XX'}^{\ddagger} + {}^3E_{HX'}^{\ddagger}] \\ \Delta D^{\ddagger} &= {}^1E_{XH}^{\ddagger} - {}^1E_{XH}^{0}\end{aligned} \tag{5b}$$

Here ${}^1E_{XH}^{\ddagger}$ and ${}^1E_{XH}^{0}$ are respectively the energies of the singlet coupled X- -H bond in the TS and the reactant state. The difference between these two quantities is given by the loss in the bond energy (the bond distortion term), $\Delta D^{\ddagger}$. ${}^3E_{XX'}^{\ddagger}$ and ${}^3E_{HX'}^{\ddagger}$ correspond respectively to the nonbonded Pauli repulsions between the $^{\bullet}$X′ and the X and H fragments of the bonded X- -H moiety.

The corresponding expressions in the Z-model[7,8] are

$$E_I^{\ddagger}(\text{Z-model}) = {}^1E_{XH}^{\ddagger} + {}^3E_{XX'}^{\ddagger} \tag{6a}$$

$$\Delta E_c(\text{Z-model}) = \Delta D^{\ddagger} + {}^3E_{XX'}^{\ddagger} \tag{6b}$$

It is apparent that both expressions (5b) and (6b) share the same bond distortion term ($\Delta D^{\ddagger}$), while they differ in the triplet repulsion terms. The Z-model, eq 6, contains only the long-range repulsion, ${}^3E_{XX'}^{\ddagger}$, but lacks the short-range repulsion ${}^3E_{HX'}^{\ddagger}$ term.

The short-range repulsion term has a fundamental physical origin.[1,13,16] Consider structure **I** in the TS, where there is a bonded X- -H species adjacent to the fragment $^{\bullet}$X′. Each of the two electrons in the bonded H- -X species has 50% α and 50% β spin, while the electron of $^{\bullet}$X′ has either α or β spin. Thus, by bringing the $^{\bullet}$X′ and the bonded H- -X to the TS geometry, the electron of $^{\bullet}$X′ feels half of a triplet repulsion with each of H and X, and this is the origin of the two repulsive terms in eq 5. The Z-model fails to account for this term, since it does not use the correct quantum chemical energy terms of structure **I**, but instead adds the redundant and improper structure **III**.

Table 1 shows the two terms, ${}^3E_{HX'}^{\ddagger}$ and ${}^3E_{XX'}^{\ddagger}$, for the series of reactions addressed in ref 1. It is apparent that the short-range repulsion term, ${}^3E_{HX'}^{\ddagger}$ is an order of magnitude, or so, larger than the long-range ${}^3E_{XX'}^{\ddagger}$ term. *It follows therefore that the dominant factor of the barrier for the identity hydrogen abstraction is the Pauli repulsion, ${}^3E_{HX'}^{\ddagger}$, across the short linkage of the TS*. In contrast, the Z-model which ignores the dominant repulsive term, ascribes the origins of the barrier to the small, ${}^3E_{XX'}^{\ddagger}$ term. The Z-model is, therefore, fundamentally deficient, and so are the related models (e.g., the BEBO model[12]) that neglect the important short-range repulsive term.[17]

Since the Z-model neglects the large repulsive term, the resonance energy term, $E_R^{\ddagger}$ (eq 4), is very small, −10.6 kcal/mol, calibrated to fit the barrier for X = H.[11] Further, $E_R^{\ddagger}$ is taken to be constant for all X's of the first two rows in the Periodic Table, and is amended to −11.6 kcal/mol for X's beyond second row.[10] In contrast, the BOVB calculations, which give reliable resonance energies,[18] show that for the identity series in ref 1, the resonance energy ($B = -E_R^{\ddagger}$) is large and variable. It is 51.1 kcal/mol for X = CH_3 and decreases down the column to 31.8 kcal/mol for X = PbH_3 (see Table 2, ref 1). It follows that the Z-model reproduces experimental barriers due to a fortuitous cancellation of errors; *it underestimates the repulsive energy at the TS and compensates by the use of a small and constant value of resonance energy*.

The breakdown of this compensation is apparent in the case of X = F, where the Z-model predicts[11] a zero barrier, while all ab initio barriers, including ones that employ extensive basis sets and high-level electron correlation treatments, are of the order of 18−20 kcal/mol.[1,19] This failure is due to the fact that the only repulsive term in the F- -H- - -F′ TS is the small long-range ${}^3E_{FF'}^{\ddagger}$ term of ca. 5.6 kcal/mol (see Table 1 here). Other cases where the Z-model succeeds[2,10,11] in predicting very low activation barrier are for X = OH, HS (RS), and Cl. In all these cases, the resulting small activation energies are fortuitous, originating in the small ${}^3E_{XX'}^{\ddagger}$ repulsion and the neglect of the very large short-range repulsion term, ${}^3E_{HX'}^{\ddagger}$ (Table 1 here).

Zavitsas criticizes eq 22 of the VB diagram model[1] for its poor performance for X = HO and HS. The basic barrier expression in the VB model, $\Delta E^{\ddagger} = \Delta E_c - B$ (eq 2 above), derives from the VB diagram in Figure 1[1] and is straightforward and rigorous. It gives rise to eq 21 (and the related eq A.9 that is identical to Malrieu's[15]). This equation expresses the barrier in terms of the promotion gap G, $G = 0.75\Delta E_{ST}(\mathrm{HX})$, which accounts for the short-range triplet repulsion. Equation 22, on the other hand, is derived from eq 21 by approximating both the gap (G) and the resonance energy (B), in terms of the bond energy, D. Equation 22 is very convenient to use *but has a limited scope due to the approximations used*. Nevertheless, it is quite helpful. For example, using the bond energy for the O−H bond (a UCCSD(T)/6-31++G** datum), this equation yields a barrier of 19.6 kcal/mol for the reaction of X = HO, compared with a barrier of 15.8 kcal/mol calculated with UCCSD(T)/6-31++G** for a linear TS structure, HO- - -H- - -OH. For X = SH, eq 22 gives a barrier of 14.8 kcal/mol while the UCCSD(T)/6-31++G** barrier is 11.0 kcal/mol. This is not a bad performance. It must be recognized, however, that in both cases, the actual TS's are not linear (our QCISD/6-31G** optimization gives an OHO angle of 138.7° and an SOS angle of 170.0°). A nonlinear TS requires more VB structures in the valence set (in Scheme 1a). These structures will make the resonance energy B larger than the value utilized in eqs 21 and 22 (e.g., $B = 0.5D$).[1] In accord, with previous calculations for the identity reaction of X = HO,[8] we find too that there exists a hydrogen-bonded cluster, HO/HOH, that precedes the TS (UCCSD(T)/6-31++G** hydrogen-bonding energy: 6.9 kcal/

mol). Moreover, the corresponding TS involves internal hydrogen bonding, where each terminal H is oriented toward the lone pair of the oxygen in the other terminus. With such features of this reaction, the success of the Z-model to reproduce the small activation energy (ca. 4.2 kcal/mol[8]) for this reaction, is more likely by chance.

In conclusion, the VB model is a physically correct model. In contrast, the Z-model ignores the true origins of the barrier. Even if its quantitative performance appears good within a limited (albeit large) set of reactions, we prefer to use a correct model and continue to improve its quantitative aspects, which at the moment are still inaccurate.

References and Notes

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