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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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Shaik et al. reported energy barrier height calculations for the title reactions.[1] Breathing orbital valence bond theory (BOVB) was used, with empirical calibrations to experimental results or semiempirical derivations of various VB factors, and the conclusion was that the calculations show that "the organizing quantity of the barriers is the singlet−triplet excitation energy (ΔE_{ST}) or bond energy (D) of the X−H bond that undergoes activation." One of the rationales for the work is given in the statement, "The involvement of the ionic structures in the transition state is associated with the polar effect which is widely discussed in the physical organic community. This effect is measured through Hammett correlations, which characterize the response of probe substituents, on the groups X and/or X′ (taken, e.g., as substituted benzyl groups) to the electron density development in the transition state."

It is not accurate that the physical organic community currently considers Hammett correlations as proof of ionic structures at the transition state (TS). We have pointed out that Hammett correlations may reflect substituent induced changes in bond dissociation energies (BDE), *not necessarily* ionic structures at the TS.[2] This proposal was subsequently confirmed experimentally for substituted phenols,[3] anilines,[4] thiophenols,[5] benzyl C−H bonds,[6] etc. Hammett correlations were obtained with BDE values for O−H, N−H, S−H, and C−H, respectively.[7] Hammett correlations of kinetic measurements of hydrogen abstractions by radicals from such compounds are influenced by corresponding changes in BDE and do not, per se, prove the importance of ionic structures at the TS. In fact, the physical organic chemistry community is currently debating the issue of the origin of substituent effects on BDE: is it an electronegativity (polar) effect *on the ground state* of the substrate or is it a stabilizing or destabilizing effect on the product radicals, $ArO^\bullet$, $ArNH^\bullet$, $ArS^\bullet$ and $ArCH_2^\bullet$?[5,8]

BOVB theory was applied to the six title reactions and extended to estimate four more (X = halogens), but experimental energies of activation are known only for two title reactions and for X = Cl. Experimental values are available for symmetrical reactions that the authors chose not to treat, e.g., X = HO, R_3CO, and RCH_2S. As a result, the credibility of conclusions from this approach is weakened. BOVB barriers are admitted not to be in agreement with experiment but such admission does not diminish the importance of this major shortcoming. In the case of X = Cl, the barrier is too high by 10.7 kcal mol^{-1} from the highest of the three experimental measurements available (none are quoted). Applying eq 22[1] to estimate the barrier for X = HO, we obtain 19.8 kcal mol^{-1}, while the experimental value is 4.2.[9] This kind of performance does not justify the claim that the calculation was "successfully applied to deduce barriers for hydrogen transfer between electronegative groups...". For $X = RCH_2S$, eq 22 gives 14.6, while experiment gives 5.2 kcal mol^{-1}. For $X = R_3CO$, eq 22 gives 17.5, while the experimental value is near 3 kcal mol^{-1}. The authors conclude, "All in all, the correspondence of the estimated barriers to the computed data are very good." Very good agreement, however, is not obtained in the real test vs experiment. The authors indicate that "numerical accuracy should be assessed against the trends rather than the individual numbers." However, there are not sufficient experimental values to establish any trends in the reactions treated. Equation 22 is used to estimate barrier heights as $\Delta E^\ddagger = 0.167 \times D(X{-}H)$, where D is *not* BDE(X−H) but bond energies computed by BOVB. For $X = CH_3$, H and SiH_3, these energies appear to be 94.2, 99.6 and 85.8 vs experimental values of 105, 104 and 92. As for trends, eq 22 predicts equal barriers for $X = CH_3$, H and R_3CO, because the (X−H) bond energy is about the same for all three. Experimental E_a values for these reactions are about 14, 10 and 3, respectively, and BOVB certainly does not reproduce this experimental trend.

Shaik et al. make no reference to other calculations of energy barriers for such reactions, such as the BEBO method[10] or our work. We have treated over one hundred hydrogen abstractions[11] by a method related to the original Heitler−London approach and the London equation,[12] which are also invoked by the authors. We also use a curve-crossing model and calculated energies of activation agree with experiment generally to within 1 kcal mol^{-1}. We find that it is *triplet repulsion between the terminal atoms* that is a major factor. For symmetrical reactions, the London equation simplifies to yield exactly this triplet repulsion term.[11e] For the five symmetrical reactions mentioned above with known E_a, our calculation agreed with an average deviation of 0.6 kcal mol^{-1} and a maximum deviation of 1.4 with $X = RCH_2S$.[11d,e,13] Shaik et al. make reference to the relation between BOVB and the "well established polar effect" as measured by Hammett correlations. The polar effect was a useful qualitative concept in its time, but is one that has been revised drastically in the last 30 years.[5,8,14] Reactions that would demonstrate polar effects are treated successfully by our calculation.[11]

Finally, the BOVB work is based on a structure set (Scheme 1)[1] placing the three electrons in eight combinations. Conspicuous by its absence is the structure with one electron on each of the three atoms (or groups). This structure is mentioned[1] in ref 40 along with the obvious requirement that the electron spins alternate up and down (↑↓↑ or ↓↑↓), but it is dismissed because the energy of this state "does not vary with distance between the atoms and hence is a nonbonded state." In fact, it is this state that gives rise to the triplet repulsion between the terminal groups, which must carry parallel spins, as also demanded by the London equation. Triplet repulsion is very much a function of distance between X and X′. The BEBO method, which is quite successful in calculating barrier heights for hydrogen abstractions,[15] also uses triplet repulsion between the terminal atoms.

References and Notes

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(14) The polar effect traces its origins to: Mayo, F. R.; Walling C. *Chem. Rev*. **1950**, *46*, 191. Shaik et al., in their ref 2,[1] have a historical error: Walling's seminal book *Free Radicals in Solution* was published in 1957, not 1973.

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