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# VBSCF Calculations on the Bimolecular (E2) Elimination Reaction. The Nature of the Transition State

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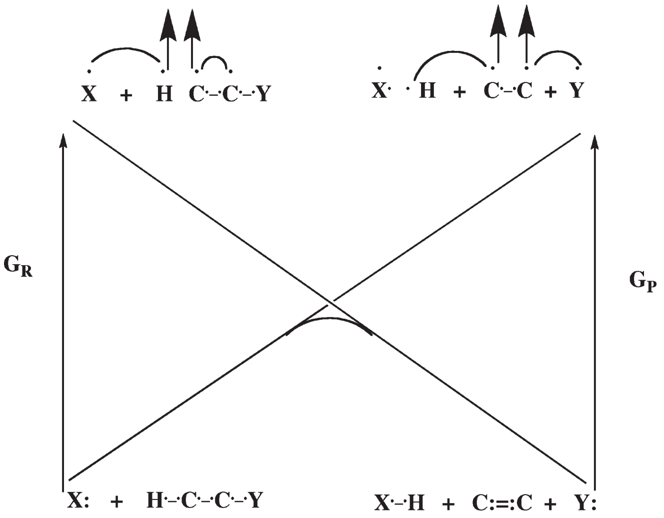

Valence bond calculations utilizing the Xiamen package have been carried out on the bimolecular (E2) elimination reaction $X^- + HCH_2CH_2Y \rightarrow XH + CH_2{=}CH_2 + Y^-$ where X,Y = F,F; F,Cl; Cl,F; Cl,Cl for *anti* and *syn* reactant complexes, transition states, and product complexes. The calculations were supplemented by MO-based calculations at MP2/6-311++G**//MP2/6-311++G**. The valence bond calculations give reasonable energies with eight contributors to the resonance hybrid. Charge-localized contributors dominate the transition states. NPA charges from the MO calculations confirm that the transition states possess a significant degree of localized charge and can be described by the key resonance structure $X(-)\text{-}H(+)\text{-}CH_2(-)\text{-}CH_2(+)\text{-}Y(-)$. At the same time, the MO calculations show that electronically and geometrically the reactions are clearly concerted though not synchronous. Valence bond state correlation diagrams (VBSCD) show that a simple proton transfer such as that in the E1cB irreversible reaction is predicted to have a lower barrier than a synchronous concerted (E2) reaction. The E2 transition state evidently avoids this energetic disadvantage by becoming localized and nonsynchronous, though with important electronic and geometric changes at all of the reacting centers.

## Introduction

We recently reported valence bond calculations on the transition state of the bimolecular elimination (E2) reaction (eq 1, B = X = F).[1] The reaction has been extensively studied.[2] While the reaction is concerted, it need not be synchronous (all electronic shifts and bond changes occurring to the same extent in the transition state). The proton transfer, for example, can take precedence over double-bond formation and loss of the leaving group. The possible paths are best represented by a More O'Ferrall−Jencks diagram[3] (Figure 1). The reactant is in the lower left and the product in the upper right corner.

$$B^- + HCH_2CH_2X \rightarrow BH + CH_2{=}CH_2 + X^- \qquad (1)$$

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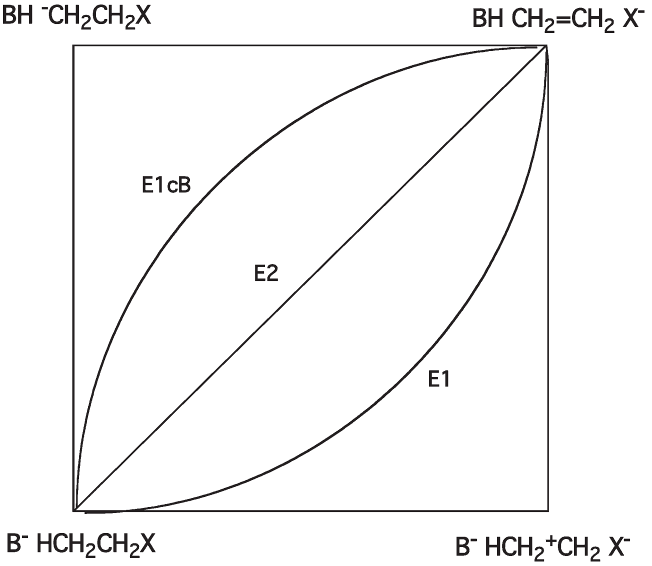

**FIGURE 1.** More O'Ferrall−Jencks diagram.

The upper left corner represents a carbanion in a stepwise reaction, and the lower right corner represents a carbocation. A synchronous reaction is represented by the straight diagonal, while a reaction with a carbanion-like transition state (but still concerted) is represented by the line that bows toward the upper left. Similarly, the line that bows toward the lower right represents a carbocation-like transition state.

Our initial expectation was that the VB hybrid of the transition state should be described by a combination of four structures analogous to the four corners of the diagram.[4] It should be emphasized that in the VB formulation of the TS these contributors must be hypothetical structures with the electron distributions of the four corners of the diagram but with a single geometry, that of the TS. These four contributors turned out to provide a completely inadequate picture of the transition state, giving an energy more than 100 kcal $mol^{-1}$ higher than that provided by a MO calculation using the same basis set.[1] A full space valence bond calculation (utilizing all structures, including those with long bonds and reversed polarities, that satisfy the rules of valence, a total of 50) did give an energy value nearly 10 kcal $mol^{-1}$ below the Hartree−Fock result, as described in ref 1. Qualitative discussions utilizing all of them would clearly be impractical, but we found that the most important eight (**1**−**8**) gave an energy below the MO value and adequately described the transition state.[1] Charge-separated contributors (**3**−**5**, **7**, and **8**), accounted for three times the weights of the other, charge-localized, structures. The TS thus exhibited a strong charge alternation with X(−)-H(+)-C-2(−)-C-1(+)-Y(−). To determine whether this pattern was general for E2 reactions or a peculiarity of the particular system (X = Y = F), we have now studied a total of eight reactions: X,Y = F,F; F,Cl; Cl,F; and Cl,Cl for both *anti* and *syn* mechanisms.

$X^-$ $H\text{-}CH_2\text{-}CH_2\text{-}Y$ **1**    $X\text{-}H$ $CH_2{=}CH_2$ $Y^-$ **2**    $X^-$ $H^+$ $^-CH_2\text{-}CH_2\text{-}Y$ **3**
$X^-$ $H^+$ $^-CH_2\text{-}CH_2{}^+$ $Y^-$ **4**    $X^-$ $HC\text{-}H_2\text{-}CH_2{}^+$ $Y^-$ **5**    $X\text{-}H$ $^-CH_2\text{-}CH_2\text{-}Y$ **6**
$X^-$ $H^+$ $CH_2{=}CH_2$ $Y^-$ **7**    $X\text{-}H$ $^-CH_2\text{-}CH_2{}^+$ $Y^-$ **8**

## Results and Discussion

The ab initio valence bond calculations were performed with XMVB.[5] It is a more recent version than the Xiamen used in ref 1 and is faster and more reliable in achieving convergence. Geometric constraints were utilized to ensure that results on the reactant complexes, the transition states, and the product complexes were comparable. The X−H−C angle was kept at 180°, and both *anti* and *syn* structures were kept periplanar. As a result of these constraints, only the *anti* transition states are fully optimized with a single imaginary frequency. The *syn* transition states have a second low-lying imaginary frequency corresponding to a torsional mode (the *syn*-periplanar conformation is not optimal), and the reactant and product complexes often show similarly low-level imaginary frequencies. The results reported in ref 1 are somewhat different from those obtained here for X = Y = F, in part because of differences in geometric constraints. However, none of the qualitative conclusions in the earlier work are affected. Preparation of the orbitals for the XMVB calculation utilized Gaussian 98.[6] MO calculations for comparison with the VBSCF results utilized either Gaussian 98 or Gaussian 03.[7] They employed the same geometric constraints as the VBSCF calculations. The models were set up and the calculations performed as previously described.[1] Orbitals from Gaussian 98 optimizations at HF/6-31+G were utilized in the XMVB calculations. The use of a modest basis set was prompted by two considerations. The first was

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**TABLE 1. Weights of Contributors at the Reactant, Product, and Transition States to the Resonance Hybrids, *anti* Elimination, $X^- + HCH_2CH_2Y$, Calculated at the VBSCF//HF/6-31+G Level**

| | X,Y = F,F | | | X,Y = F,Cl | | |
|---|---|---|---|---|---|---|
| structure | reactant | TS | product | reactant | TS | product |
| **1** | 0.201 | 0.105 | 0.001 | 0.287 | 0.033 | 0.000 |
| **2** | 0.000 | 0.123 | 0.348 | 0.001 | 0.071 | 0.369 |
| **3** | 0.187 | 0.068 | 0.014 | 0.277 | 0.065 | 0.004 |
| **4** | 0.282 | 0.327 | 0.020 | 0.194 | 0.319 | 0.030 |
| **5** | 0.309 | 0.049 | 0.015 | 0.204 | 0.153 | 0.010 |
| **6** | 0.003 | 0.021 | 0.007 | 0.004 | 0.007 | 0.002 |
| **7** | 0.014 | 0.275 | 0.596 | 0.028 | 0.302 | 0.579 |
| **8** | 0.005 | 0.127 | −0.003 | 0.004 | 0.050 | 0.005 |

| | X,Y = Cl,F | | | X,Y = Cl,Cl | | |
|---|---|---|---|---|---|---|
| structure | reactant | TS | product | reactant | TS | product |
| **1** | 0.245 | 0.005 | 0.000 | 0.342 | 0.006 | 0.000 |
| **2** | 0.000 | 0.265 | 0.491 | 0.000 | 0.233 | 0.497 |
| **3** | 0.181 | 0.012 | 0.000 | 0.255 | 0.012 | 0.000 |
| **4** | 0.233 | 0.207 | 0.051 | 0.160 | 0.226 | 0.050 |
| **5** | 0.325 | 0.065 | 0.013 | 0.217 | 0.074 | 0.009 |
| **6** | 0.001 | 0.004 | 0.000 | 0.001 | 0.002 | 0.000 |
| **7** | 0.014 | 0.317 | 0.411 | 0.023 | 0.365 | 0.407 |
| **8** | 0.002 | 0.125 | 0.033 | 0.002 | 0.082 | 0.036 |

**TABLE 2. Weights of Contributors at the Reactant, Product, and Transition States to the Resonance Hybrids, *syn* Elimination, $X^- + HCH_2CH_2Y$, Calculated at the VBSCF//HF/6-31+G Level**

| | X,Y = F,F | | | X,Y = F,Cl | | |
|---|---|---|---|---|---|---|
| structure | reactant | TS | product | reactant | TS | product |
| **1** | 0.205 | 0.013 | 0.000 | 0.303 | 0.110 | 0.000 |
| **2** | 0.000 | 0.059 | 0.356 | 0.000 | 0.028 | 0.366 |
| **3** | 0.195 | 0.087 | 0.000 | 0.292 | 0.223 | 0.000 |
| **4** | 0.311 | 0.457 | 0.052 | 0.217 | 0.327 | 0.052 |
| **5** | 0.279 | 0.043 | 0.009 | 0.179 | 0.130 | 0.007 |
| **6** | 0.002 | 0.039 | 0.000 | 0.004 | 0.031 | 0.000 |
| **7** | 0.003 | 0.107 | 0.565 | 0.002 | 0.100 | 0.554 |
| **8** | 0.004 | 0.194 | 0.017 | 0.004 | 0.051 | 0.020 |

| | X,Y = Cl,F | | | X,Y = Cl,Cl | | |
|---|---|---|---|---|---|---|
| structure | reactant | TS | product | reactant | TS | product |
| **1** | 0.280 | 0.001 | 0.000 | 0.361 | 0.022 | 0.000 |
| **2** | 0.000 | 0.322 | 0.492 | 0.000 | 0.024 | 0.497 |
| **3** | 0.205 | −0.003 | 0.000 | 0.268 | 0.018 | 0.000 |
| **4** | 0.243 | 0.152 | 0.051 | 0.182 | 0.323 | 0.050 |
| **5** | 0.273 | 0.111 | 0.013 | 0.190 | 0.296 | 0.009 |
| **6** | 0.000 | −0.002 | 0.000 | 0.001 | 0.001 | 0.000 |
| **7** | −0.002 | 0.362 | 0.412 | −0.002 | 0.307 | 0.407 |
| **8** | 0.000 | 0.058 | 0.032 | 0.001 | 0.010 | 0.036 |

that we wished to make a clean separation between active and inactive orbitals. We avoided basis sets with d orbitals to prevent the mixing of the active orbitals in the xz plane with orbitals having y components. The other reason was to keep the computational time low because the time required for VBSCF calculations rises rapidly with the number of basis functions. As before,[1] the active electrons were the eight in the bonds undergoing change in the course of the reaction plus one unshared pair each on the base (X) and on the leaving group (Y) for a total of 12. All $p_y$ and all inner-shell electrons were frozen. The nonreacting hydrogen orbitals were confined to the plane of the reacting bonds by taking linear combinations, $H_1 + H_2$ and $H_3 + H_4$.

Weights of the contributing structures calculated for the reactant complexes, the transition states, and the product complexes are shown in Tables 1 and 2.

The reasonableness of the weights can be tested by a few key comparisons. Weights of structures putting a negative charge on the base **X** (**1** + **3** + **4** + **5** + **7**) sum to nearly 1 for the reactant complexes, and weights of structures putting a negative charge on the leaving group **Y** (**2** + **4** + **5** + **7** + **8**) sum to nearly 1 for the product complexes. For the transition states, both of these numbers are significantly less than 1, showing that charge has been donated from the base to the substrate, and the leaving group is in the process of becoming a negative ion. The reactions thus show the characteristics expected for a concerted E2 process. Are they synchronous, in the sense that the changes occurring between the reactant and the transition state have progressed to approximately the same extent?

While concerted, these reactions cannot be characterized as synchronous. A completely synchronous hybrid would utilize only the reactant-like (**1**) and the product-like (**2**) contributors. But these two together add up to only 5−32% of the eight-structure hybrid, with most below 20%. These two, along with **6**, are the only structures that preserve maximum covalent bonding. Structures with charges localized on three or all five reacting atoms (**3** + **4** + **5** + **7** + **8**) are heavily weighted (68−95%) in the transition state—more heavily than in the reactant or product complexes except for X = Cl, Y = F, a reaction that is strongly endothermic. Structures with negative charge on C-2 (**3** + **4** + **6** + **8**) are likewise strongly weighted in the transition state. Yet the transition state cannot be described simply as being E1cB-like (left of the diagonal in Figure 1). Weights of structures with a double bond (**2** + **7**) are in all cases appreciable (0.37−0.60 for *anti* eliminations, 0.13−0.68) for *syn*). These numbers would be even higher if structures accounting for the C-1(+)-C-2(−) polarization of the bond were included. Structures putting a negative charge on the leaving group increase in weight from reactant complex to transition state. The TS is thus not intermediate in electron distribution between the reactant complex and the product complex. It is more heavily polarized than either, with substantial charge localization on the reacting atoms. While the charge on the base is delocalized into the substrate in the transition state, the resulting charge distribution is very uneven with increased negative charge on C-2 and Y but increased positive charge on H. The charge on C-1 sometimes becomes more negative, sometimes more positive.

These conclusions from the weights are well supported by Gaussian calculations at a rather high level (MP2/6-311++G**//MP2/6-311++G**) NPA charges[8] from these calculations are listed in Table 3. Charge transfer from the base is accompanied by charge buildup on both C-2 and the leaving group, and there is strong charge alternation along the reacting atoms (X(−), H(+), C-2(−), C-1(+), Y(−)). Again, the picture is of a reaction that is concerted but with major charge localization on the reacting atoms, not the smoothed out electron distribution expected for a synchronous TS. We next consider the manner in which these characteristics vary with stereochemistry and the nature of X and Y. For this discussion, the bond distances (Table 4) and energies (Tables 5 and 6) of reactant complexes, transition states, and product complexes are useful.

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**TABLE 3.** NPA Atomic Charges (MP2/6-311++G**//MP2/6-311++G**) at the Reactant, Product, and Transition States in E2 Reactions of $X^- + HCH_2CH_2Y$

| atom | reactant | TS | product | reactant | TS | product |
|---|---|---|---|---|---|---|
| | X,Y = F,F *anti* | | | X,Y = F,Cl *anti* | | |
| X | −0.964 | −0.664 | −0.637 | −0.960 | −0.777 | −0.619 |
| H | 0.335 | 0.576 | 0.583 | 0.341 | 0.482 | 0.583 |
| $C_2$ | −0.611 | −0.721 | −0.614 | −0.590 | −0.784 | −0.532 |
| $C_1$ | 0.193 | 0.024 | −0.079 | −0.227 | −0.127 | −0.191 |
| Y | −0.488 | −0.856 | −0.944 | −0.201 | −0.416 | −0.964 |
| | X,Y = Cl,F *anti* | | | X,Y = Cl,Cl *anti* | | |
| X | −0.985 | −0.405 | −0.319 | −0.983 | −0.563 | −0.306 |
| H | 0.274 | 0.299 | 0.289 | 0.278 | 0.301 | 0.283 |
| $C_2$ | −0.577 | −0.635 | −0.525 | −0.554 | −0.696 | −0.486 |
| $C_1$ | 0.190 | −0.022 | −0.024 | −0.245 | −0.010 | −0.231 |
| Y | −0.475 | −0.919 | −0.991 | −0.170 | −0.751 | −0.994 |
| | X,Y = F,F *syn* | | | X,Y = F,Cl *syn* | | |
| X | −0.964 | −0.644 | −0.611 | −0.957 | −0.740 | −0.603 |
| H | 0.335 | 0.597 | 0.584 | 0.357 | 0.524 | 0.581 |
| $C_2$ | −0.318 | −0.550 | −0.220 | −0.312 | −0.575 | −0.171 |
| $C_1$ | 0.434 | 0.328 | 0.236 | 0.037 | 0.116 | 0.185 |
| Y | −0.488 | −0.731 | −0.989 | −0.125 | −0.324 | −0.992 |
| | X,Y = Cl,F *syn* | | | X,Y = Cl,Cl *syn* | | |
| X | −0.987 | −0.397 | −0.319 | −0.986 | −0.546 | −0.306 |
| H | 0.291 | 0.320 | 0.289 | 0.289 | 0.316 | 0.283 |
| $C_2$ | −0.274 | −0.467 | −0.205 | −0.241 | −0.422 | −0.157 |
| $C_1$ | 0.408 | 0.330 | 0.226 | 0.037 | 0.279 | 0.174 |
| Y | −0.439 | −0.786 | −0.991 | −0.099 | −0.628 | −0.994 |

**TABLE 4.** Bond Distances (Å) (MP2/6-311++G**//MP2/6-311++G**) in E2 Reactions of $X^- + HCH_2CH_2Y$

| bond | reactant | TS | reactant | TS |
|---|---|---|---|---|
| | X,Y = F,F *anti* | | X,Y = F,Cl *anti* | |
| $H-C_2$ | 1.13 | 1.72 | 1.13 | 1.43 |
| $C_2-C_1$ | 1.50 | 1.37 | 1.51 | 1.44 |
| $C_1-Y$ | 1.43 | 2.01 | 1.82 | 2.00 |
| | X,Y = Cl,F *anti* | | X,Y = Cl,Cl *anti* | |
| $H-C_2$ | 1.10 | 1.91 | 1.10 | 1.53 |
| $C_2-C_1$ | 1.50 | 1.36 | 1.51 | 1.38 |
| $C_1-Y$ | 1.42 | 2.20 | 1.81 | 2.38 |
| | X,Y = F,F *syn* | | X,Y = F,Cl *syn* | |
| $H-C_2$ | 1.13 | 1.93 | 1.13 | 1.51 |
| $C_2-C_1$ | 1.53 | 1.39 | 1.53 | 1.46 |
| $C_1-Y$ | 1.40 | 1.76 | 1.80 | 1.94 |
| | X,Y = Cl,F *syn* | | X,Y = Cl,Cl *syn* | |
| $H-C_2$ | 1.10 | 1.90 | 1.10 | 1.86 |
| $C_2-C_1$ | 1.52 | 1.38 | 1.53 | 1.38 |
| $C_1-Y$ | 1.40 | 1.86 | 1.79 | 2.56 |

The charge donated from the base, X, to the substrate ranges from 0.18 to 0.59 units. The smallest values for both *anti* and *syn* reactions are for X = F, Y = Cl. These reactions are the only exothermic ones (Table 5). The charge gains by Y are correspondingly small, the two sets of figures together indicating an early transition state. For X = Cl, Y = F, the reactions are strongly endothermic, indicating a late transition state. The charge gain by Y, however, is smaller than the charge donated by X. The net negative charge increase on the carbon skeleton is shared by C-2 and C-1. When X = Y = Cl, charge donation from X is intermediate, but charge gain by Y is the largest of any of the transition states. In these cases, C-2 becomes more negative in the transition state but C-1 becomes more positive. The charge donation from X does not differ much from *syn* to *anti* except for X = Y = Cl, but the charge gain by Y is smaller for *syn* than for *anti*, suggesting a more carbanion-like transition state.

**TABLE 5.** Energies (kcal $mol^{-1}$) at MP2/6-311++G**// MP2/6-311++G** Relative to Reactant Complex

| System | *anti* TS | *anti* product | *syn* TS | *syn* product |
|---|---|---|---|---|
| F,F | 14.82 | 14.23 | 29.3 | 2.41 |
| F,Cl | 6.22 | −8.72 | 5.86 | −21.41 |
| Cl,F | 48.44 | 47.17 | 43.71 | 36.69 |
| Cl,Cl | 31.58 | 23.20 | 32.02 | 12.37 |

**TABLE 6.** Energies (kcal $mol^{-1}$) at VBSCF/6-31G//HF/6-31G Relative to Reactant Complex

| system | *anti* TS | *anti* product | *syn* TS | *syn* product |
|---|---|---|---|---|
| F,F | 30.45 | 12.44 | 16.94 | −10.21 |
| F,Cl | 17.82 | −27.12 | 21.39 | −48.30 |
| Cl,F | 66.39 | 49.32 | 70.23 | 36.95 |
| Cl,Cl | 39.87 | 11.88 | 47.78 | −1.80 |

The bond distances confirm that the transition states lie geometrically between the reactant and product complexes, with all bonds undergoing significant changes in length between the reactant complex and the transition state. Particularly noteworthy is the TS C-2 to C- 1 bond length, which in most cases is closer to a double bond than to a single bond value. The only exception is the X = F, Y = Cl reaction. We noted above that this transition state is probably early because the reaction is exothermic. There is no consistent pattern to bond length differences between the *anti* and *syn* transition states.

The bond distances are clearly consistent with a concerted reaction in which all reacting bonds have changed substantially in the TS from their values in the reactant complexes. The H−C-2 bond has lengthened by 0.30−0.81 Å, and the C−Y bond by 0.18−0.78. The C-1−C-2 bond has shortened to nearly the value in the product complexes (1.34−1.36 Å), the only exception being the bond in the F,Cl transition state. In this case, the C−H and C−Cl extensions are small, indicating a more reactant-like transition state than for the other reactions.

Tables 5 and 6 show substantial differences between MP2 and VBSCF energy values. A linear least-squares plot of the VBSCF vs the MP2 energies shows a reasonable linear correlation with a correlation coefficient, *R*, of 0.968. The trends in the two sets of energies are thus similar. The MP2 values employ a much more flexible basis set and so were used in qualitative discussions. The energies listed are all with respect to the energies of the corresponding reactant complexes as zero. The activation energies are substantial, particularly so for the *anti* and *syn* Cl,F transition states. The *syn* reactions have higher activation energies than the *anti* except for the F,F case. Most of the reactions are endothermic, especially the *anti* and *syn* Cl, F reactions that combine a poor leaving group with a weak base.

The overall picture from our calculations is of transition states that are definitely concerted in the sense of having reacting bonds that are substantially different in length from the corresponding bonds in the reacting complexes and that are changing in directions leading toward bond lengths in the product complexes. The changes in electron distribution from reactant complex to transition state to product complex are clearly not smoothly synchronous. That transition state charges are significantly localized on the reacting centers goes against the assumption common in many mechanistic discussions that electron delocalization leads to lower energy states. This assumption is well founded for stable conjugated systems but must be rethought for transition states.

Comparison of these results with experiment is difficult for several reasons. The reactions are in the gas phase, and the reactants are much simpler structures than those used in most experimental investigations. Various aspects of transition-state structure can be probed experimentally by structure−reactivity correlations and isotope effects,[2] but there have been few really comprehensive efforts to place transition states on More O'Ferrall−Jencks diagrams (Figure 1). Particularly thorough approaches are found in the work of Jencks' group probing the E2−E1cB borderline. They found that reactions of a number of 2-arylethyl and 2-cyanoethyl derivatives gave transition states near the upper left corner of the figure, in some cases into stepwise E1cB territory.[9] In comparison, the transition states in our investigation seem all to be moderately left of the diagonal in the figure, ranging from reactant-like for F,Cl to product-like for Cl,F and F,F. The experimental results give no direct evidence on our main finding that charge localization on the reacting atoms is substantial.

Elimination reactions bear a definite resemblance to cases of nonperfect synchronization occurring in deprotonation of substrates that lead to delocalized anions.[10] MP2 calculations support the experimental evidence pointing to a build-up of negative charge in the transition state on the carbon atom being deprotonated. Though the most noteworthy feature of the calculations is the buildup of charge on carbon, the rest of the substrate also undergoes significant changes in the transition state. In the identity reaction transfer of a proton from acetaldehyde to acetaldehyde enolate, for example, the negative charge on oxygen increases from −0.632 in acetaldehyde to −0.804 and the carbon−oxygen bond lengthens by 0.032 units in the transition state.[10c] Both of these changes are a little more than half of the corresponding changes from acetaldehyde to acetaldehyde enolate. These reactions, too, are clearly concerted in that all reacting atoms and bonds are changing in the transition state from their reactant values, even though the changes occur nonsynchronously.

We have been interested for some time in why systems showing nonperfect synchronization choose to avoid a synchronous process which would appear intuitively to provide greater electron delocalization and hence lower energy.[10d] The generally accepted explanation was first advanced by Kresge,[11] who suggested that charge transferred from the base to the acceptor atom could not be fully delocalized because rehybridization was incomplete in the transition state. As a qualitative argument this is plausible, though it leaves open the question of why rehybridization is not more extensive if it could result in more delocalization and a lower energy. Our VBSCF study of the identity reaction of acetaldehyde with acetaldehyde enolate reveals the resonance contributors responsible for incomplete delocalization, the most important one being a low-energy triple ion $\mathbf{A^- H^+ A^-}$. Analogous contributors in the present results, the triple ion **3** and the alternate charges structure **4**, are important. There is thus little doubt that charge localization is favorable in the transition states of these reactions. The intriguing question is whether there is some fundamental quantum-chemical principle involved.

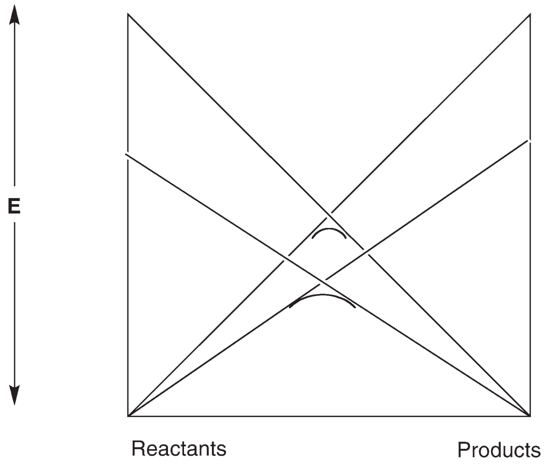

**FIGURE 2.** VB diagram for simple vs multibond reactions.

The VB theory of chemical reactions offers a possible resolution. Dewar[12] argued that multibond reactions were likely to be inherently more difficult than simple atom transfers. His argument received little attention at a time when so-called "zipper" mechanisms were popular. The basis of his contention is illustrated in Figure 2.

The barrier to reaction is constructed from the interaction of curves representing the reactant and product electron distributions, respectively. The "curves" are shown as straight lines in this and subsequent figures for the sake of simplicity and to avoid prejudging the actual curvature in a particular case. When the geometry of the reactant changes toward that of the product while the electron distribution remains that of the reactant, the energy rises, and similarly for the energy of the product in the reverse direction. Where these curves intersect resonance interaction occurs, resulting in a barrier below the intersection point. When a simple atom transfer is involved, the main contribution to the rise in energy will be the stretching of one bond (lower curves). In a multibond reaction, however, two or more bonds will be stretching, resulting in a steeper rise in energy (upper curves), a higher intersection point, and hence, a higher barrier.

At about the same time, Shaik and Pross were applying a more quantitative version of this formalism[13] using a VB model developed previously.[14] This version utilizes VB state correlation diagrams (VBSCD).[15] Figure 3 is such a diagram for an E1cB reaction with the first step rate determining. It is thus equivalent to a simple proton transfer. The diagram for this case is constructed as follows. The reactant state is raised to an excited state of the same geometry (vertical transition) that correlates down to the product ground state. The energy

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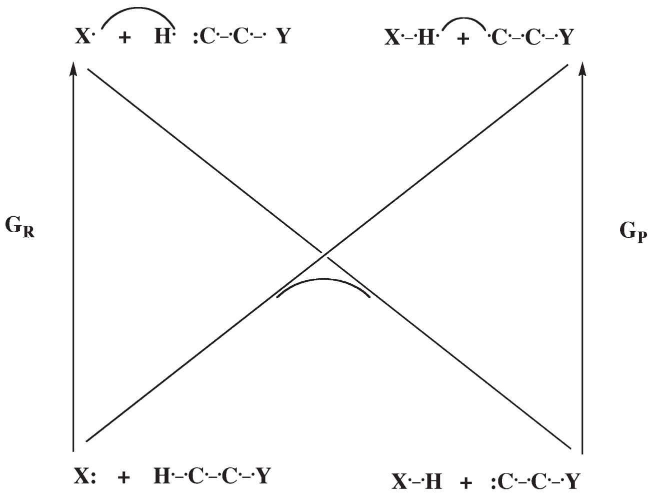
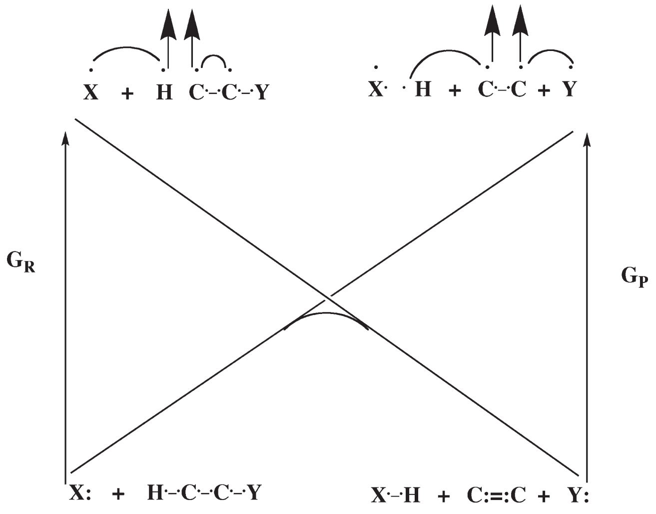


$G_R$ = IP(X:) - EA(CH) )

$G_P$ = IP(C:) - EA(XH)

**FIGURE 3.** VBSCD for E1cB reaction, first step slow.



$G_R$ = IP(X:) - EA(CY) + $\Delta E_{ST}$(CH)

$G_P$ = IP(Y:) - EA(XH) + $\Delta E_{ST}$(C=C)

**FIGURE 4.** VBSCD for an E2 reaction.

**TABLE 7. Data for *G* Value Calculations (kcal mol$^{-1}$)**

| quantity | *E*(HF/6-31G) | *E*(VBSCF/6-31G) |
|---|---|---|
| IP($Cl^-$) | 51 | 51 |
| IP($F^-$) | −6 | −6 |
| EA($CH_3$-Cl) | −84 | −93 |
| EA($CH_3$-F) | −146 | −147 |
| $DE_{st}$($CH_3$-H) | 272 | 284 |
| $DE_{st}$($H_2C{=}CH_2$) | 84 | 92 |
| EA($CH_3$-H) | −155 | −169 |
| EA(Cl-H) | −84 | −150 |
| EA(F-H) | −124 | −215 |
| IP($H_3C:^-$) | −45 | −69 |

of the excited state above the ground state results from two processes: the removal of an electron from the base X and the insertion of this electron into an antibonding orbital of the C−H bond. The energy required is $G_R$, consisting of the ionization potential of X: minus the electron affinity of C−H. In the reverse direction the energy required is $G_P$, wherein an electron must be removed from C: and donated to the X−H bond. The point where the curves cross in the middle is the location of the transition state. Its energy will be lower than the crossing point by resonance energy, *B*. The crossing point energy is some fraction, $f < 1$, of $G_R$. The activation energy, $E_A$, is then given by eq 2. Thus, $E_A$ is proportional to $G_R$, and $G_R$ values for related reactions should be in the same order as the activation energies.

$$E_A = fG_R - B \qquad (2)$$

In a synchronous E2 reaction the C−H bond is broken and an X−H bond formed, but in addition a C−C double bond is formed and a C−Y bond is broken. The VBSCD for this case is given by Figure 4. Now an electron from X: is transferred to the C−Y bond, and the breaking of the C−H bond is prepared by raising the electron pair to a triplet state. $G_R$ now has three terms instead of two. In the reverse direction, an electron from Y: is transferred to the X−H bond and the double bond is raised to a triplet state to prepare for the necessary rebonding. Thus, $G_R$ and $G_P$ each have an additional term compared to the same quantities for the E1cB reaction.

This observation strongly suggests that the *G* values will be larger for a synchronous E2 reaction than for an analogous E1cB reaction and that the "putative" E2 reaction will be slower than an E1cB reaction with the same base and leaving group. In the absence of specific numbers for the ionization potentials, electron affinities, and singlet−triplet gaps required to evaluate *G*, we cannot be certain that activation energies will always be larger for concerted E2 than E1cB reactions. But values for these vertical transition energies in the literature are few. In order to get a consistent set of values, we chose calculation. At first glance, it would seem that the simple models needed could easily be calculated at a very high MO level. It is not that easy, for we want electrons to come from (ionization potentials) or go into (electron affinities) specific bonding or nonbonding orbitals. But with very flexible basis sets, the transitions are more likely to involve diffuse orbitals. Consequently, we chose simple HF/6-31G basis sets for Hartree−Fock and VBSCF calculations on simple models. Table 7 shows the results.

In most cases, the agreement between the two sets of values is adequate for our qualitative purposes. Where there are substantial differences we place more trust in the VBSCF values, for the VBSCF method gives somewhat more control over where in the molecule the electrons come from or go to.

As it turns out, concern over which set of values is more reliable is unnecessary. Table 8 shows the calculated values of $G_R$ and $G_P$ using VBSCF//HF/6-31G (first number in each entry) and HF/6-31G (number in parentheses). Clearly, both $G_R$ and $G_P$ in all cases are much larger for the E2 than for the E1cb reactions. While the differences will doubtless be attenuated in the $E_A$ value ($f < 1$ in eq 2), there can be little doubt that a synchronous E2 reaction labors under an energetic disadvantage compared to an analogous E1cB reaction. The fraction *f* need not be the same for the E2 and E1cB

**TABLE 8.** *G* Values (kcal mol$^{-1}$) at the VBSCF//HF/6-31G[a] Level

| system | E2 fwd | E2 back | E1cB fwd | E1cB back |
|---|---|---|---|---|
| F,F | 425 (412) | 301 (202) | 163 (149) | 146 (79) |
| F,Cl | 371 (350) | 358 (259) | 163 (149) | 146 (79) |
| Cl,F | 482 (469) | 236 (162) | 220 (206) | 81 (39) |
| Cl,Cl | 428 (407) | 293 (219) | 220 (206) | 81 (39) |

[a] The first number is the value at VB/6-31G; the number in parentheses is the value at HF/6-31G.

reactions, but it is unlikely that it could be so different as to override the gaps of ca. 100−200 kcal mol$^{-1}$ between the *G* values.

But elimination reactions normally prefer a concerted pathway in the absence of strong activation at C-2 and/or a very poor leaving group at C-1.[2] The apparent contradiction can be resolved by the evidence presented in this work and elsewhere that E2 reactions are very nonsynchronous. They thus avoid all or most of the energetic disadvantage of the synchronous pathway. In addition, they can take advantage of the energy gained by partial double bond and X−H bond formation in the transition state. This must be an important factor judging from the high degree of double bond character suggested by the short C-1 to C-2 bonds (vide supra). These features arise from the mixing of the high-lying covalent and partially covalent VB structures into the charge-alternated structure. That these C-1−C-2 bonds are polarized in the transition state should not adversely affect the stabilization. In the VB treatment of ethylene, the energy is lowered by inclusion of the two equivalent $CH_2^+$-$CH_2^-$ contributors.[16] Solvation effects undoubtedly play a role for reactions in solution. The highly polarized transition states must be more effectively solvated than synchronous ones would be.

VBSCD's can also be constructed for other reactions that show nonperfect synchronization such as the deprotonation of acetaldehyde and propene. They are similar to Figure 4 in showing more terms than those found in simple deprotonations (Figure 3). We have not calculated for them the quantities contributing to $G_R$ and $G_P$, but given the decisive differences shown in Table 8, it is highly probable that these reactions, too, eschew synchronicity for the same reasons as the E2 reaction does.

**Acknowledgment.** We thank Changwei Wang for carrying out the VB calculations on which the data in Table 7 are based.

**Supporting Information Available:** Energies, partial VBSCF outputs, and **Z**-matrices showing the optimized geometries used in the VBSCF calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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