

# A Qualitative Valence-Bond Approach to Organic Reactivity. Application to Elimination Reactions

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**Abstract:** A general method for building up the reaction profile for the entire range of elimination reactions, using simple valence-bond configurations, is described. Rules which enable the method to be applied to any organic reaction are presented. The approach enables predictions to be made regarding the nature of the transition state, the possible intervention of intermediates along the reaction pathway, and the effect of substituent changes on rates and reaction mechanism. Application of the model to elimination reactions leads to conclusions in general agreement with current views. A number of new features, however, are observed. For example, the possibility of an elimination mechanism not yet observed, involving a radical-anion intermediate, is deduced, and a theoretical justification for the E2C-E2H mechanism is presented. Also, the concertedness of C-H and C-X bond cleavage in proper E2 substrates is questioned.

## Introduction

The importance of recognizing and understanding the factors responsible for governing chemical reactivity is evident. It is clear that without such understanding the ability of the chemist to predict and organize problems of reactivity is severely handicapped.

It is true that quantum mechanical calculations, at whatever level of sophistication, may be capable of providing specific answers to specific problems. However, the calculations, by their very complexity, often do not provide a general insight and conceptualization of a broad area.

What the chemist would like to have is a theoretical framework in which he can conceptualize some of the central questions of reactivity: what are the factors which govern the makeup of a reaction profile or the height of the energy barrier, and when can one expect an intermediate to be generated during the course of the reaction?

To achieve such a conceptual appreciation, one must search for a way in which to qualitatively define the makeup of a reaction profile. A significant step in this continuing search was made by the introduction of potential energy surfaces models.<sup>1-5</sup> The most prominent of these were proposed by Thornton,<sup>1</sup> More O'Ferrall,<sup>2</sup> Harris and Kurz,<sup>3</sup> Critchlow,<sup>4</sup> and Jencks.<sup>5</sup> All these models have one important feature in common: they provide the chemist with a qualitative means of estimating the effect of substituents on the structure and energy of the transition state.<sup>6</sup> In addition, they bring together under one unifying mechanistic scheme the entire mechanistic range in substitution (S<sub>N</sub>2-S<sub>N</sub>1) and elimination reactions (E1-E1cB-E2).<sup>7</sup>

Despite the obvious progress brought about by these models, we believe a general quantum mechanical model, which can be

utilized to methodically construct a potential energy curve for any reaction, is lacking. Such a model should be able to answer the following questions: (a) Why does a reaction barrier arise and how large will it be? (b) What is the nature of the transition state? (c) Will an intermediate be formed? (d) How will substituents affect (a)-(c)?

The approach we use is to build up the potential energy curve from its component building blocks. This is done in much the same way as a qualitative theorist constructs a delocalized orbital from its building-block fragment orbitals (the PMO method).<sup>8</sup> There is some flexibility in the choice of building blocks. One possible choice is the D-A (donor-acceptor) approach in which one constructs the potential curves from configurations based on reactant (one D, the other A) states such as the no-bond DA, and the charge-transfer, D<sup>+</sup>A<sup>-</sup>, states. This approach was utilized by Mulliken,<sup>9a-c</sup> Nagakura,<sup>9d</sup> and Epiotis and Shaik.<sup>10</sup> Subsequently Shaik<sup>11</sup> has shown that using this method one can derive one basic principle for all organic reactions involving at least one closed-shell reactant. In these reactions, the reaction profile arises from an avoided crossing of two configurations. Thus, reaction potential curves are composed of two branch components, one ascending and describing the reactant bonds, and the other descending and describing the product bonds. In all cases, the ascending branch is the ground-state no-bond configuration DA, while the descending branch originates from an excited configuration (e.g., D<sup>+</sup>A<sup>-</sup>, D<sup>\*</sup>A<sup>\*</sup>, etc., depending on the type of reaction).<sup>11</sup> Thus, the closed-shell reactants are prepared for bonding through the generation of *spin-paired* odd electrons in reactant orbitals which are symmetry matched.

A second choice is to use VB structures as building blocks for constructing reaction profiles. This approach was used in the early

(1) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

(2) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274.

(3) Harris, J. C.; Kurz, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 349.

(4) Critchlow, J. E. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 1774.

(5) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(6) For recent reviews on transition state structure, see: (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) More O'Ferrall, R. A. In "The Chemistry of the Carbon Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Vol. 2, p 609. (c) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705. (d) Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354. (e) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (f) Albery, W. J. *Prog. React. Kinet.* **1967**, *4*, 355. (g) Bruice, T. C. *Annu. Rev. Biochem.* **1976**, *45*, 331. (h) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69. (i) McLennan, D. J. *Tetrahedron* **1975**, *31*, 2999. (j) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755.

(7) For an analysis of the S<sub>N</sub>2 reaction using the potential energy surface models, see: (a) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1354. (b) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; Chapter 5. (c) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295. For an analysis of elimination reactions using the potential energy surface models, see (d) ref 2. (e) Winey, D. A.; Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102. (f) Lewis, D. E.; Sims, L. B.; Yamataka, H.; McKenna, J. *Ibid.* **1980**, *102*, 7411.

(8) For reviews on the PMO method, see: (a) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley-Interscience: New York, 1976. (b) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1. (c) Klopman, G., Ed. "Chemical Reactivity and Reaction Paths"; Wiley-Interscience: New York, 1974. (d) Hudson, R. F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 36. (e) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975.

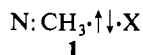
(9) The donor-acceptor formalism was first introduced by Mulliken; see (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801. (c) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. See also, (d) Nagakura, S. *Tetrahedron, Suppl.* **2** **1963**, *19*, 361.

(10) (a) Epiotis, N. D.; Shaik, S. In "Progress in Theoretical Organic Chemistry"; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1977; Vol. 2. (b) Epiotis, N. D.; Shaik, S. *J. Am. Chem. Soc.* **1977**, *99*, 4936. (c) Epiotis, N. D.; Shaik, S. *Ibid.* **1978**, *100*, 1, 9, 29. (d) Shaik, S.; Epiotis, N. D. *Ibid.* **1978**, *100*, 18. (e) Epiotis, N. D.; Shaik, S.; Zander, W. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980. (f) Epiotis, N. D. "Theory of Organic Reactions"; Springer-Verlag: Heidelberg, 1978.

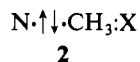
(11) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692.

days of quantum mechanics by Evans and Polanyi and Laidler and Shuler.<sup>12</sup> More recently Warshel and Weiss<sup>13</sup> have applied a similar approach to compare reactions in solutions and in enzymes.

Actually, as was shown by one of us,<sup>11</sup> the two choices of building blocks are analogous. Thus, in the D-A format, the  $S_N2$  reaction profile arises from a  $DA-D^+A^-$  avoided crossing, whereas in the VB method the main two forms which partake in the avoided crossing are a reactant-like form:



and a product-like form:



where the odd electrons in each case are spin-paired.

These two forms turn out to be the main VB components of DA and  $D^+A^-$ , respectively. Thus, one can qualitatively describe the ascending branch of the  $S_N2$  potential curve either by DA or by the VB form 1 and the descending branch by  $D^+A^-$  or by the VB form 2.

In most cases, it is best to use the D-A and the VB formalisms in conjunction. In this manner one does not lose important features which may be more readily exposed by just one of them. For example, factors which determine the preferred orientation of the reactants and the role of orbital symmetry are most readily accessible using the D-A format.<sup>10,11</sup> This blended approach was utilized by us<sup>14</sup> in analyzing substituent effects in  $S_N2$  reactions of benzyl derivatives.

In this paper we would like to continue our search for means of conceptualizing reactivity problems through the construction of potential energy curves for elimination reactions. This is done with the aim of showing how one can account for the entire spectrum of E1-E2-E<sub>1c</sub>B reactivity, to clarify the E2C-E2H controversy and to suggest a novel mechanism which possibly leads to elimination.

Elimination reactions are not easily analyzed in the D-A format. This is because the acceptor moiety in elimination reactions is the alkyl derivative and the bonding changes take place at three quite different sites within the alkyl derivative: the C-H bond, which is broken, a C=C bond which is formed, and a C-X bond which is broken. Thus, in elimination reactions, alkyl derivatives have no simple acceptor orbital in contrast to the  $S_N2$  reaction which was previously analyzed,<sup>14</sup> where the bonding changes in the alkyl group occur in the C-X bond only. Therefore, we will not use the D-A approach here but will construct the potential curves using just VB structures.

We, of course, recognize our approach to be a gross simplification of the mathematical analysis. However, its important advantage is that it is conceptually clear and contains within it the essence of a quantum mechanical treatment. Above all, as we shall show, this approach is very "chemical" in nature and thus enables one to obtain an intuitive feel of how a given system is likely to respond to a given perturbation. We believe that only through a qualitative model, which is necessarily simple, does that feeling of chemical insight and understanding come to the fore.

## Theory

**A. The Chemical Bond.** The qualitative VB method can be described as a thermochemical quantum method. Its two main variables are the energy differences of VB forms from which the reaction potential curve is generated, and the energy changes of these VB forms due to the molecular distortions along the reaction coordinate. The energy of the VB forms is readily equated with

thermochemical quantities such as bond energies, ionization potentials, and electron affinities. Accordingly, the energy changes of the VB forms along the reaction coordinate can be discussed in terms of changes in these thermochemical quantities. The central concept of the VB approach is the "bond", and naturally, this is the pivot about which all our arguments will revolve. We begin, therefore, by summarizing the nature of chemical bonds using VB terminology.<sup>15a</sup>

The structure AX, where A and X are either atomic or molecular units, may be represented by a number of VB forms. Let us first consider the two-electron forms. The form  $A \cdot \uparrow \downarrow \cdot X$  represents a wave function with two spin-paired electrons: one electron is associated with group A, and one with group X. Thus  $A \cdot \uparrow \downarrow \cdot X$  symbolizes the Heitler-London type wave function, as shown in eq 1.<sup>16</sup> Such a wave function, of course, constitutes

$$A \cdot \uparrow \downarrow \cdot X \equiv 2^{-1/2} \{ |\phi_A(1)\bar{\phi}_X(2)| - |\bar{\phi}_A(1)\phi_X(2)| \} \quad (1)$$

a simple description of the *covalent bond* since, as Heitler and London<sup>17</sup> illustrated 50 years ago, the energy corresponding to this wave function, and taking into account nuclear repulsion, leads to a minimum at a short bond distance and hence to bond formation. Thus, it is only the *spin-paired* form (eq 1) which leads to a covalent two-electron bond. There is another form, the positive combination of the two determinants of eq 1, which describes the triplet pair,  $A \cdot \uparrow \uparrow \cdot X$ . This wave function is repulsive with respect to A--X approach.

The form A: X represents a wave function in which two spin-paired electrons are situated on A and none on X. Thus:

$$A: X \equiv |\phi_A(1)\bar{\phi}_A(2)| \quad (2)$$

Similarly, the second form is:

$$A: X \equiv |\phi_X(1)\bar{\phi}_X(2)| \quad (3)$$

In organic compounds these two forms (eq 2 and 3) are high-energy forms and they constitute the excited states of the two-electron bond  $A \cdot \uparrow \downarrow \cdot X$  (eq 1). This is because forms such as A: X are generally zwitterionic and exhibit electrostatic minima at long distances.<sup>10b,f,18</sup> For example, the form  $H_3C^+ : F^-$  is ~6.5 eV higher in energy than the form  $H_3C \cdot \uparrow \downarrow \cdot F$ .

The most accurate description of a polar covalent two-electron bond will involve a mixture of all three possible configurations,  $A \cdot \uparrow \downarrow \cdot X$ , A: X, and A: X. Thus while A: X and A: X do not, in themselves, lead to bond formation, mixing them into the Heitler-London  $A \cdot \uparrow \downarrow \cdot X$  form will improve the description of the covalent bond formed. The improved wave function,  $\psi$ , is described by eq 4.

$$\psi \simeq A \cdot \uparrow \downarrow \cdot X + \lambda_1(A: X) + \lambda_2(A: X) \quad (4)$$

From this point on we shall describe the covalent bond A-X by the form  $A \cdot \uparrow \downarrow \cdot X$ ,<sup>16</sup> though we recognize the secondary weight of the zwitterionic forms in the wave function of the bond. We adopt the main form of the bond as the sole descriptor for qualitative purposes. However, the reader must recall that this choice is a matter of convenience and simplicity and that the two-electron bond is really described by eq 4.

The three-electron forms of AX may be represented by A: X and A: X. In this case the wave functions describing each of these forms lead to energies higher than those of the separate entities.<sup>15b</sup> Again it is the linear combination,  $\psi$  (eq 5), which leads to a stable

$$\psi = (A: X) + \lambda(A: X) \quad (5)$$

three-electron bond, whose stability increases for A = X. In

(12) (a) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11. (b) Evans, M. G.; Warhurst, E. *Ibid.* **1938**, *34*, 614. (c) Evans, M. G. *Ibid.* **1939**, *35*, 824. (d) Laidler, K. J.; Shuler, K. E. *Chem. Rev.* **1951**, *48*, 153. (e) Laidler, K. J. "The Chemical Kinetics of Excited States", Clarendon Press: Oxford, 1955.

(13) Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6218.

(14) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.

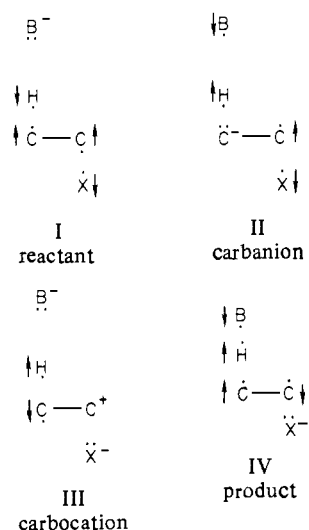
(15) (a) For a detailed discussion, see: Pauling, L.; Wilson, E. B. "Introduction to Quantum Mechanics"; McGraw-Hill: New York, 1935. (b) This is demonstrated for  $He_2^+$  in ref 15a, p 360.

(16) While we choose to represent the Heitler-London wave function pictorially as  $A \cdot \uparrow \downarrow \cdot X$ , one must remember that it is properly represented as a linear combination of the two spin-paired forms:  $A \cdot \uparrow \downarrow \cdot X$  and  $A \cdot \uparrow \downarrow \cdot X$ .

(17) Heitler, W.; London, F. Z. *Phys.* **1927**, *44*, 455.

(18) (a) Salem, L.; Rowlands, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317.

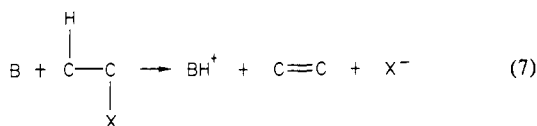
Scheme I



resonance terms, one can say that the structure  $\text{A} \leftrightarrow \text{X}$  may be stable owing to the resonance contributions:



**B. Potential Energy Curves for Elimination Reactions.** Having summarized the nature of the interaction between two groups A and X as a function of the number of electrons in the wave functions associated with A and X, we can now tackle the problem of building up a reaction profile. The key element here is the concept that the reaction profile may be generated from a linear combination of appropriate VB structures, each representing, in chemical form, a specific wave function. We will illustrate this concept in detail below. First, then, let us seek out the VB structures we will need to define the reaction profile of an elimination reaction. The appropriate VB forms for a general elimination reaction:



are illustrated in Scheme I. Let us examine each of these configurations and their corresponding energies as a function of the (assumed) reaction coordinate. Configuration I is termed the reactant configuration. This is because the key bonding electrons are distributed among the reacting atoms in a way that defines the reactants. Thus we have interactions between B:, H:, C—C, and X·. Between B: and H· there is no bonding since this constitutes a repulsive three-electron interaction. The interactions between C<sub>β</sub> and H as well as between C<sub>α</sub> and X are bonding, however, because both interactions correspond to the Heitler-London  $\text{A} \uparrow \downarrow \text{X}$  form (eq 1).

Let us now examine the effect of changing the geometry on the energy of configuration, I. Specifically, what we want to know is how will the energy of the configuration change as the geometry of the reaction complex changes from reactant-like to product-like.

The reactant configuration, I, will move up in energy as the geometry of the reaction complex proceeds along the reaction coordinate. This is illustrated in Figure 1. This occurs because a C—H and a C—X bond (both represented as  $\text{A} \uparrow \downarrow \text{X}$ ) are being broken while a repulsive three-electron interaction is generated between B: and ·H. In other words, all the geometric changes characteristic of the transformation lead to an increase in energy of the reactant configuration, I.

The product configuration, IV, on the other hand, at the reaction starting point, is at relatively high energy. In fact, it describes a double electron excitation relative to I; i.e., it involves two electronic promotions. First, an electron in the base has been transferred to the leaving group. Thus the C—X interaction,

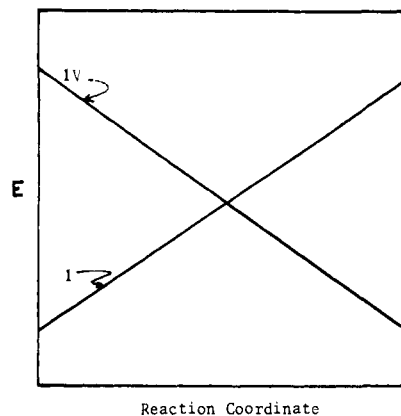


Figure 1. Energy of reactant configuration, I, and product configuration, IV, along the assumed reaction coordinate.

initially described in the reactant by  $\text{C} \uparrow \downarrow \text{X}$ , now becomes  $\text{C}:\text{X}$  and therefore repulsive in character. Secondly, it describes the unpairing of C—H bond electrons and thereby the cleavage of this bond.<sup>19,20</sup> These two processes place IV initially above I.

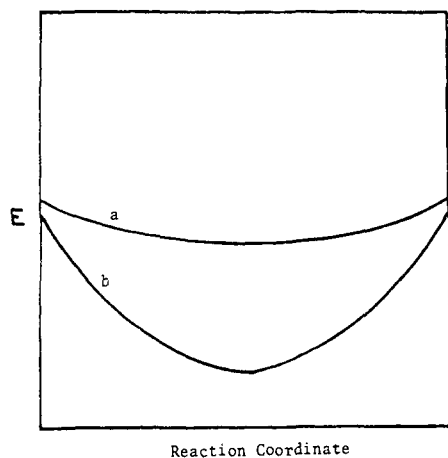
The only favorable interaction present in IV which was absent in I is the  $\text{B} \cdot \downarrow \text{H}$  interaction. However, this interaction is, as yet, not realized because early along the reaction coordinate the B—H distance is still large, thus precluding bond formation. As the reaction proceeds, however, and the structure of the reaction complex increasingly resembles products, the product configuration, IV, drops in energy (Figure 1) since B—H bonding can now occur, the repulsive C—X interaction is diminished because of X<sup>-</sup> moving away, and a double bond between the two carbons finally takes form. It is now apparent why we term configuration I the reactant configuration and IV the product configuration. Configurations I and IV are thus the key configurations which describe the reactants and products, respectively.

The number of additional possible VB configurations which may be constructed is considerable since the problem becomes one of determining all possible ways of distributing six valence electrons about five atomic centers. At this point, however, we must let chemical principles guide our choice of configuration building. We must seek out chemically "sensible" configurations whose energies are sufficiently low so as to allow them to play a part in generating the reaction profile. Since both carbanions and carbocations are on occasion formed in elimination reactions, these are the most likely configurations. The carbanion configuration, II, and the carbocation configuration, III, are illustrated in Scheme I. Let us now analyze the forms of the energy curves for these two configurations, noting that they are quite different from those for reactant and product configurations (I and IV).

Before we can describe the carbanionic curve, II, it should be pointed out that the form of the curve is dependent on the nature of the reaction coordinate. So we will describe the energy curve for two separate cases. The first pathway we consider is for the case in which approximately synchronous cleavage of the C—H and C—X bonds occurs. Under these conditions the carbanionic curve will be relatively flat. Initially II is higher than I since an electron has been transferred from B: to C, leading to B· and C<sup>-</sup>, and to the generation of the unstable three-electron form, C:·H. As the reaction proceeds the energy of II drops owing to the formation of the B—H bond and the release of the repulsive

(19) Both I and IV contain four electrons in four different atomic orbitals or hybrids. Such VB wave functions are described by four determinants which together constitute a *singlet* spin-adapted wave function:  $\frac{1}{2}[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta]$ . Thus we can see that the first and second pairs of electrons are triplet pairs, whereas electrons 14 and 23 are spin paired. In the reactant configuration, I, the spin-paired electrons are across the C—H and C—X moieties, which make both proper two-electron bonds, whereas in IV the spin-paired electrons are across the B—H and the C=C moieties, which now makes them the two-electron bonds.

(20) Rules for spin adaptation can be found inter alia in: McGlynn, S. P.; Vanquickenborne, L. G.; Kinoshita, M.; Carroll, D. G. "Introduction to Applied Quantum Chemistry"; Holt, Rinehart and Winston: New York, 1972; Chapter 7.



**Figure 2.** Energy of carbanion configuration, II, along the reaction coordinate, for the case where (a) C-H and C-X bond cleavage are concerted, (b) C-H bond cleavage precedes C-X bond cleavage.

C:H interaction. This will be counteracted by the energy rise which is imposed by stretching the C-X bond. Whenever such a situation with two opposing trends is obtained, the resulting curve is likely to be relatively flat, as shown in Figure 2, curve a.

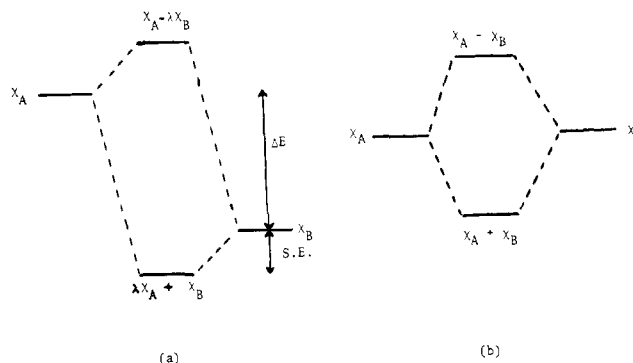
Now we consider a reaction coordinate where C-H bond breaking is ahead of C-X bond breaking. Here the curve initially descends markedly owing to B-H formation and the release of the repulsive C:H interaction. Only further along the reaction coordinate, as the C-X bond starts to break, does the curve rise, thereby leading to the formation of a rather deep minimum (Figure 2, curve b). The shape of the carbanionic curve will be similar to that of the carbanionic curve in that it also is likely to exhibit a shallow curve and a deep minimum, respectively, in the two possible reaction modes—the synchronous E2 and the stepwise E1 pathways.

So far we have not considered the effect of solvation on the curves, and it may now be appropriate to comment on this point. In general, the solvent will not change the shape of the curves but will stabilize all points along any curve which describes charged species. Thus, I will be stabilized mostly at the reaction starting point when B: is a charged base (e.g., HO<sup>-</sup>), whereas IV will be stabilized mostly at the reaction final point because of the solvation of X<sup>-</sup>. On the other hand, II and III will be stabilized throughout, but mostly at the reaction final point. This action of the solvent will make the minima of the corresponding curves shallower, but more importantly it may have a profound impact on the course of the reaction by making these intermediates accessible to the ground surface.<sup>21</sup>

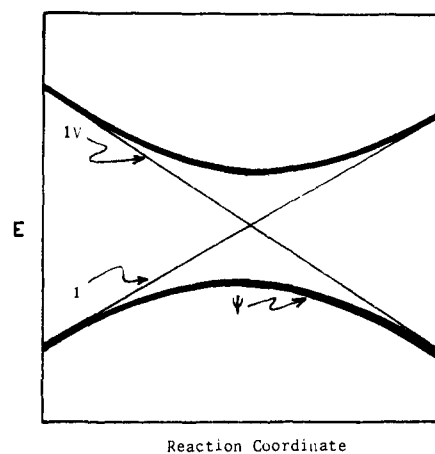
Having described our basis configurations and how their energies vary along the reaction coordinate, we can now turn to examining the reaction characteristics of elimination reactions using the configurations just described as building blocks. Let us first illustrate the basic approach using just two configurations, the reactant configuration, I, and the product configuration, IV. With just these two configuration energy curves, we can construct a simplified reaction profile. The key element in this construction is the concept that *at any point along the reaction coordinate the reaction complex is described by a linear combination of the basis set configurations*. Thus, for the simplified case of just two configurations:

$$\psi = C_1\chi_1 + C_{IV}\chi_{IV} \quad (8)$$

where  $\psi$  is the reaction complex wave function and  $\chi_1$  and  $\chi_{IV}$  represent wave functions describing configurations I and IV, respectively, and  $C_1$  and  $C_{IV}$  refer to their corresponding coefficients. The rules for mixing configurations are essentially the same as those for mixing orbitals. *When two configurations mix, the bonding combination is stabilized while the antibonding com-*



**Figure 3.** Interaction diagram for two configurations,  $\chi_A$  and  $\chi_B$ , leading to two states, a stabilized bonding combination and a destabilized antibonding combination when (a) the two configurations are separated by an energy gap,  $\Delta E$ , and (b) the two configurations are degenerate.



**Figure 4.** Formation of the reaction profile,  $\psi$  (bold curve), from the reactant configuration, I and product configuration, IV.

*ination is destabilized.* This is illustrated in Figure 3a. The stabilization energy, SE, is proportional to the square of the matrix element,  $\langle \chi_A | H | \chi_B \rangle$  and inversely proportional to the energy gap when the latter is wide enough. This is shown in eq 9. The

$$SE = \langle \chi_A | H | \chi_B \rangle^2 / \Delta E \quad (9)$$

configuration matrix element  $\langle \chi_A | H | \chi_B \rangle$  is roughly the matrix element of those orbitals within  $\chi_A$  and  $\chi_B$  which differ in one-electron occupancy.<sup>10</sup> In the case of configurations I and IV, the relevant atomic orbitals are the orbitals of B and X, since B: in I becomes B· in IV and X· in I becomes X: in IV. Thus:

$$\langle \chi_I | H | \chi_{IV} \rangle \approx \langle \phi_B | H | \phi_X \rangle \quad (10)$$

where  $\phi_B$  and  $\phi_X$  represent the atomic wave functions on B and X, respectively. Since this term is strongly dependent on the overlap between  $\phi_B$  and  $\phi_X$ , it is often approximated by:

$$\langle \phi_B | H | \phi_X \rangle = K S_{BX} \quad (11)$$

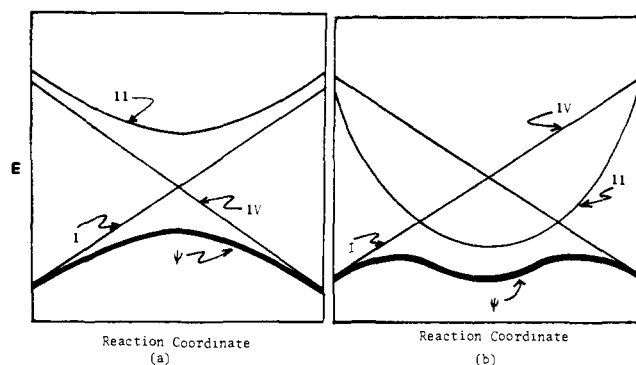
where  $S_{BX}$  is the overlap between the orbitals  $\phi_B$  and  $\phi_X$  and  $K$  is some energy constant.

The extent to which the less stable configuration,  $\chi_A$  (Figure 3a), mixes into  $\chi_B$ , as defined by the mixing parameter,  $\lambda$ , is given by:

$$\lambda = \langle \chi_A | H | \chi_B \rangle / \Delta E \quad (12)$$

Expressed in words, eq 12 states that the extent to which a high-energy configuration mixes into a low-energy configuration is proportional to the overlap (recall  $\langle \chi_A | H | \chi_B \rangle = K S_{AB}$ ) and inversely proportional to the energy gap. When the two configurations become degenerate, eq 11 and 12 are not valid. The interaction is then simply given by the matrix element  $\langle \chi_A | H | \chi_B \rangle$ , and the two states  $\chi_A + \chi_B$  and  $\chi_A - \chi_B$  split by twice this quantity as shown in Figure 3b.

(21) For a description of how ion pairs arise in solvolyses, see: (a) ref 10b, (b) ref 10f, (c) ref 9c, and (d) ref 13.



**Figure 5.** Formation of the reaction profile,  $\psi$  (bold curve), from the reactant configuration, I, the carbanionic configuration, II, and the product configuration IV for (a) a concerted E2-E1cB pathway, (b) for an E1cB pathway with formation of a carbanion intermediate.

Now that we have stated the rules which govern configuration mixing, we can construct a reaction profile for the elimination reaction using just the two configurations I and IV. This is shown in Figure 4. At the reaction starting point the wave function,  $\psi$ , describing the reaction complex will be almost entirely described by  $\chi_I$ . This is because the energy gap between I and IV is, at this point, large and the overlap between the orbitals  $\phi_B$  and  $\phi_X$  small. As we proceed along the reaction coordinate the energy gap between  $\chi_I$  and  $\chi_{IV}$  decreases and the overlap between them increases. As a result the stabilization energy increases (from eq 9) and  $\chi_{IV}$  mixes increasingly into  $\chi_I$  (from eq 12). At the intended curve crossing between  $\chi_I$  and  $\chi_{IV}$  these two functions are equal in energy and at that point each contributes approximately equally to  $\psi$ , the wave function for the reaction complex. At this point the stabilizing interaction is greatest. As one proceeds further, the reaction complex is now described primarily by  $\chi_{IV}$ , which is the more stable configuration in the later stages of the reaction coordinate.

We see that what occurs, therefore, is that the mixing of the two configuration curves generates two new curves. It is the lower of these two curves which will define the ground-state reaction pathway. The upper curve will define an excited-state reaction pathway and will not concern us further. The present model thus provides us directly with information concerning the transition state. Since the transition state is composed of a reaction complex described about equally by  $\chi_I$  and  $\chi_{IV}$  (i.e.,  $C_I$  and  $C_{IV}$  (eq 8) are approximately equal), the structure of the transition state will reflect the relative contributions of the two contributing configurations. This means that the B-H bond and the C=C double bond will be approximately 50% formed, and the C-X bond about 50% cleaved. Such a transition state clearly describes that for a central E2 reaction pathway. This will be true, however, only if the curve is indeed composed of just  $\chi_I$  and  $\chi_{IV}$ . In practice, more than two configurations may be involved though, of course, reactant and product configurations are of prime importance. Let us examine how the intervention of either the carbanion, II, or carbocation, III, configurations affects the argument.

For the case in which the carbanion configuration, for example, is sufficiently stable to mix into the reactant and product configuration, the reaction complex wave function will now be described by:

$$\psi = C_I\chi_I + C_{II}\chi_{II} + C_{IV}\chi_{IV} \quad (13)$$

As a consequence the reaction profile will take on carbanionic character. Two general cases may be considered. (a) The carbanionic configuration is higher in energy than the reactant and product configurations in the vicinity of the transition state. This is illustrated in Figure 5a. For such a case the profile followed is a one-step pathway in which the transition state takes on carbanionic character to an extent determined by the coefficient  $C_{II}$  in eq 13 at the transition state. Thus we will expect a transition state with advanced C-H bond cleavage, a partial negative charge on  $C_\beta$ , and only slight C-X bond cleavage. This is just the

E2-E1cB-type mechanism and is anticipated for substrates containing carbanionic stabilizing groups (e.g., phenyl on  $C_\beta$ ). (b) If very strongly carbanion-stabilizing groups are present, the carbanionic configuration, II, will now be displaced to lower energy, to the extent that it may (with solvent fortification) actually be more stable than the reactant and product configurations near their intended crossing point. This is seen in Figure 5b. In such a case, an intermediate will be generated whose structure will be determined primarily by the carbanionic configuration. This is because the carbanionic configuration, being the most stable one, will lead to a large  $C_{II}$  value in eq 13. On this basis, we can clearly classify the intermediate as a "carbanion" though the manner in which it is generated makes it apparent that different carbanions are likely to differ in structure to some extent (because of the slight mixing of additional configurations).

We conclude, therefore, that the carbanion intermediate is generated by the intended crossing of the reactant configuration, I, with the carbanionic configuration, II. Product formation is governed by the intended crossing of the carbanion configuration, II, with the product configuration, IV. The reversible or irreversible character of the carbanion intermediate will be governed by the precise shape of configuration II: specifically which of the two maxima of Figure 5b will be higher in energy and hence which of the two steps will be rate determining.

The preceding arguments for the carbanion configuration, II, can be used in exactly the same way for the carbocation configuration, III. Thus a figure analogous to Figure 5a will represent a concerted E2-E1 pathway while one such as that in Figure 5b will represent an E1 mechanism in which a carbocation intermediate is generated. We see, therefore, that through the configuration mixing approach the entire E1-E2-E1cB spectrum is readily generated.

**C. Rules for Determining the Reaction Profile and the Nature of the Transition State.** Let us now summarize the basic ideas governing the configuration mixing model.

- (1) The reaction profile is generated from a linear combination of VB configurations.
- (2) Two key configurations are those describing reactants and products. Additional configurations are obtained by seeking out chemically "sensible" intermediates.
- (3) The reaction complex at any point along the reaction coordinate, including the transition state, will be described by a mixture of VB configurations in proportion to their relative stability. Configurations of low energy will mix into the complex more than configurations of high energy.
- (4) The reaction mechanism and hence the reaction coordinate will, themselves, be governed by the nature of the configurations from which the profile is built up. Thus, for example, a large contribution of the carbonium configuration will endow the entire reaction coordinate with E1 character.
- (5) The character of the transition state will reflect the extent to which the configurations mix into its wave function. Thus, in general, the transition state will be endowed with the characteristics of the configurations of lowest energy in the vicinity of the transition state.

(6) An intermediate is likely to be formed in a reaction whenever the configuration describing that intermediate is similar or lower in energy than reactant and product configurations in the region of the transition state.

(7) Stabilization of any configuration through a substituent (or solvent) effect will lead to an energy lowering of the entire reaction profile and to the transition state acquiring more of the character of that configuration. By character we generalize: geometric features and charge distribution. Thus, in general,  $A \cdot \uparrow \downarrow \cdot X$  structures with two electrons prefer tight  $A \cdots X$  contact, whereas  $A \cdot \uparrow \downarrow \cdot X$ ,  $A \cdot \uparrow \cdot X$  (and  $A \cdot X$ ), and  $A \cdot X$  prefer loose  $A \cdots X$  contact.

#### Application

On the basis of the VB configuration method just described, we now approach some of the questions concerning elimination reactions which have been of considerable mechanistic interest over the past 2 decades.<sup>22</sup>

**A. Effects on Mechanism.** The factors governing the mechanistic pathway in elimination reactions are now quite well understood and only relatively subtle points remain controversial. Nonetheless, it is instructive to examine in passing how the reaction pathway of elimination reactions can be understood through use of the VB configuration model, and to focus on the additional insight this model offers.

We have already noted that a central E2 mechanism will be anticipated when the key interacting configurations are the reactant and product configurations, I and IV. An E2-E1cB or an E1cB pathway will result when the carbanion configuration, II, is relatively stabilized compared to IV. Similarly, an E2-E1 or an E1 pathway will result when the carbocation configuration is stabilized.

What are the factors, therefore, that will stabilize the carbanionic, II, and carbocationic III, configurations relative to the product configuration, IV? Inspection of II indicates it will be relatively stabilized, if (a) electron-withdrawing substituents on  $C_\beta$ , which are carbanion stabilizing, are introduced (e.g., *p*-nitrophenyl), and (b) leaving groups with strong C-X bonds are used (e.g., F). Inspection of III indicates it will be relatively stabilized if (a) electron-releasing groups on  $C_\alpha$ , which are carbocation stabilizing, are introduced (e.g., *p*-methoxyphenyl), and (b) a weak base is used (stabilizing B: compared to B· which appears in the product configuration). Thus we conclude that carbanion-stabilizing groups and poor leaving groups will move the reaction toward the E1cB end of the spectrum<sup>22c</sup> while carbocation-stabilizing groups and weak bases will tend to encourage the E1 end of the spectrum. These conclusions are in accord with both experiment and current thinking.<sup>22</sup>

**B. Orientation.** It is well known that elimination reactions can yield in certain cases either the least substituted olefin (Hofmann orientation) or the most substituted olefin (Saytzeff orientation).<sup>23</sup> Within the VB model the configurations which mix into the transition state and which will ultimately determine the orientation are the carbanionic configuration, II, and the product configuration IV. The carbocationic configuration, III, does not directly affect the orientation since this configuration makes no distinction between the  $C_\beta$  hydrogens on either side of  $C_\alpha$ .

Based on the VB approach the reason for two possible orientations now becomes apparent and conforms entirely with currently held views. If the transition state has a large component of the carbanionic configuration, II, then if two such possible configurations exist (i.e., because of the possibility of carbanion formation on either side of  $C_\alpha$ ) clearly the most stable configuration will predominate. Since it appears, at least in solution, that the least substituted carbanion is the most stable one, mixing of the carbanionic configuration, II, into the transition state will lead to Hofmann orientation. For the case where the predominant configuration in the transition state is the product one, IV, then the primary consideration will be the stability of the  $\dot{C}$ -C interaction (see configuration IV, Scheme I) or, in other words, the relative stability of the possible C=C bonds. Since the most substituted double bond is known to be thermodynamically the most stable (because of hyperconjugative interactions), such elimination reactions will encourage Saytzeff orientation.

For the case that the transition state is dominated by the carbocationic configuration, III (i.e., an E1 pathway), then orientation will be governed by the curve that III will intend crossing in order to generate product. Since this is almost certainly the product configuration, IV, in the case of an E1 pathway, and not the carbanionic configuration, II, we conclude that the E1 pathway

will also lead to preferential Saytzeff orientation.

Much of the above discussion is just a brief summary of how the VB model reproduces conclusions agreed upon by most investigators in the field. Now we will illustrate how the model offers some new insight into aspects which are less well understood.

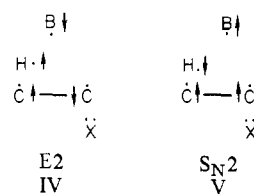
**C. Effect of Base Strength.** There is clear evidence that in elimination reactions an increase in base strength leads to a more carbanionic transition state. This appears to be true for the entire E2-E1cB range.<sup>22k</sup> For example, in the elimination reaction of a series of  $ArCH_2CH_2Br$ , using phenoxide ion as a base, a  $\rho$  value of 2.64 was obtained. For the case of a weaker base, *p*-nitrophenoxide ion, a smaller  $\rho$  value of 1.84 was observed.<sup>22k,24</sup> The larger  $\rho$  value in the case of the stronger base usually means greater negative charge on  $C_\beta$  and hence more C-H bond breaking. The generality of this behavior is illustrated by the fact that similar conclusions have been reported for the more carbanion-activating system,  $Ar_2CHCCl_3$ ,<sup>25</sup> as well as the unactivated system, 2-iodobutane.<sup>26</sup>

Examination of the configurations in Scheme I indicates that an increase in base strength will stabilize the carbanionic configuration, II, and the product configuration, IV, relative to the other configurations. However, the effect of II will be more important than that of IV. This is because II will be relatively more stabilized by a given perturbation of the base strength than the intersection point of I and IV.<sup>27</sup> As a result the dominant effect of II leads to the prediction of *more* carbanionic character in the transition state in accord with experiment (rule 5).

It is of interest to note that the potential energy surface models<sup>1-5</sup> provide a less clear-cut prediction regarding the effect of base strength. Assuming equal parallel and perpendicular effects leads to a prediction of little change in the degree of C-H bond breaking, and consequently little change in the carbanionic character of the transition state.

**D. E2C-E2H Spectrum.** The configuration mixing model throws new light on a subject that has remained somewhat controversial over the past decade—the existence of an E2C-E2H mechanistic spectrum. The key issue here concerns the contention first proposed by Parker and Winstein<sup>28</sup> that in elimination reactions, catalyzed by weak bases of high nucleophilicity, the transition state involves a loose interaction between the base and  $C_\alpha$ .<sup>29</sup>

One of the features of the E2C mechanism is its obvious resemblance to the  $S_N2$  reaction. Let us see, therefore, the relation between the product configurations leading to E2 and  $S_N2$  pathways. The two configurations which are shown below both



(24) (a) Alunni, S.; Baciocchi, E. *Tetrahedron Lett.* **1973**, 4665. (b) Alunni, S.; Baciocchi, E.; Mancini, V. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1866.

(25) (a) McLennan, D. J.; Wong, R. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1818. (b) Jackson, O. R.; McLennan, D. J.; Short, S. A.; Wong, R. J. *Ibid.* **1972**, 2308.

(26) (a) Bartsch, R. A.; Pruss, G. M.; Bushaw, B. A.; Wiegiers, K. E. J. *Am. Chem. Soc.* **1973**, *95*, 3405. (b) Bartsch, R. A.; Wiegiers, K. E.; Guritz, D. M. *Ibid.* **1974**, *96*, 430.

(27) The transition state is made up from the mixing of the subsidiary configurations into the intersection point. Since the intersection point is a resonance hybrid of I and IV, any stabilization of IV will only be partially reflected in the stabilization of the intersection point. For example, if I and IV are mimicked by two straight lines with slopes  $\pm 1$ , then the stabilization of the intersection point is 0.5 of that of IV, while if I and IV are represented by two parabolas this fractional stabilization reduces to 0.25. On the other hand, the relative flatness of II means that essentially all the stabilization of II will express itself in the vicinity of the transition state.

(28) (a) Beltrame, P.; Biale, G.; Lloyd, D. J.; Parker, A. J.; Ruane, M.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2240. (b) Parker, A. J.; Ruane, M.; Palmer, D. A.; Winstein, S. *Ibid.* **1972**, *94*, 2228.

(29) For reviews on this controversy, see (a) ref 22b, (b) ref 22h. See also (c) Bunnett, J. F.; Eck, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 1897, 1900.

(22) For recent reviews on the mechanism of elimination reactions, see: (a) Saunders, W. H.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley-Interscience: New York, 1973. (b) McLennan, D. J. *Tetrahedron*, **1975**, *31*, 2999. (c) McLennan, D. J. *Q. R. Chem. Soc.* **1967**, *21*, 490. (d) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19. (e) Bunnett, J. F. *Surv. Prog. Chem.* **1969**, *5*, 53. (f) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225. (g) Bordwell, F. G., *Acc. Chem. Res.* **1972**, *5*, 374. (h) Ford, W. T. *Ibid.* **1973**, *6*, 410. (i) Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200. (j) Ref 5b. (k) Baciocchi, E. *Acc. Chem. Res.* **1979**, *12*, 430. (l) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453.

(23) Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 408.

involve four electrons in four different atomic orbitals or hybrids. They differ, however, in their spin-pairing pattern and therefore in their degree of electronic promotion with respect to the reactant configuration I (Scheme 1).

Both configurations involve an electron transfer from the base to the leaving group X, but they differ in the degree of electronic promotion in the C<sub>β</sub>-H bond. In the S<sub>N</sub>2 configuration, V, the C---H interaction is described by two spin-paired electrons, and, thus, it remains unchanged with respect to the C-H bond in I. On the other hand, the C---H interaction in the E2 configuration, IV, appears as a triplet pair, and thus it describes an excitation of the C-H bond relative to its state in the reactant configuration, I. Therefore, at the reaction starting point, the E2 configuration, IV, is higher in energy than the S<sub>N</sub>2 configuration, V.

Let us now consider the elimination reaction profile with inclusion of the S<sub>N</sub>2 configuration, V, without at this point attempting to answer the question: why do we get elimination products at all if the E2 configuration, IV, starts higher in energy than the S<sub>N</sub>2 configuration, V?

First let us consider how the energy of the S<sub>N</sub>2 configuration, V, changes along the elimination reaction coordinate. The main stabilizing factor is the release of the repulsive three-electron interaction, C·:X, as X<sup>-</sup> departs, as well as a favorable B·↑↓·C<sub>α</sub> interaction as the base approaches the substrate. This stabilization is counteracted by the destabilization involved in stretching the C-H bond. The net result of these opposing trends consists of a relatively flat curve. We can now distinguish between two distinct cases. The first case shown in Figure 6a covers a wide spectrum of reactivity but its main feature is that the S<sub>N</sub>2 type configuration is close to the I-IV intended crossing point, which is in the vicinity of the transition state.

Recalling rule 5 that any configuration which mixes into the transition state endows the activated complex with its characteristic features, we conclude that the activated complex in Figure 6a will be endowed with considerable S<sub>N</sub>2 character. What is this character? Inspection of V reveals that part of the stabilization of the S<sub>N</sub>2 curve arises from the B·↑↓·C<sub>α</sub> interaction. This interaction is not present in either I or IV and only the mixing of the S<sub>N</sub>2 configuration will be responsible for its induction into the activated complex. When the mixing becomes substantial, it will be reflected in the structure of the transition state, and the base will be accommodated so as to enjoy the additional stabilizing interaction with C<sub>α</sub>. Thus such a transition state may be represented by the following structure:



$$\psi_{\text{TS}} = C_{\text{IXI}} + C_{\text{IVXIV}} + C_{\text{VXV}}$$

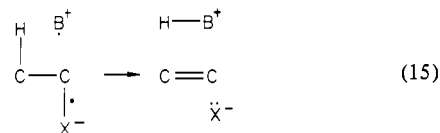
The B---H interaction derives from configuration IV while the B---C interaction derives from configuration V. Consequently, the extent of these two interactions will be dependent on the relative magnitudes of coefficients C<sub>IV</sub> and C<sub>V</sub>. A large C<sub>IV</sub> coefficient will represent an E2H pathway while a large C<sub>V</sub> coefficient will represent an E2C pathway. Clearly, the entire E2C-E2H spectrum is now readily generated as C<sub>IV</sub> and C<sub>V</sub> values vary.

It is now clear why for E2C reactions rates correlate with S<sub>N</sub>2 rates and not basicities,<sup>30</sup> and low k<sub>H</sub>/k<sub>D</sub> isotope effects<sup>31</sup> (indicating little C<sub>β</sub>-H bond breaking) were observed. Configuration V will clearly encourage S<sub>N</sub>2 reactivity patterns and discourage C<sub>β</sub>-H bond-breaking (rule 4). Thus the E2C mechanism will be observed whenever the C<sub>β</sub>-H bond is strong, the base is of low basicity but of high nucleophilicity (e.g., SH<sup>-</sup>), the C-X bond is a good electron acceptor, and most importantly when the S<sub>N</sub>2

pathway is precluded (generally owing to steric congestion). It is only when these conditions are met that the reactant configuration, I, rises up steeply (cleavage of a strong C-H bond) and the product E2 configuration, IV, descends slowly (weak B-H bond) so that the S<sub>N</sub>2 configuration, V, will remain close to the intended crossing point and will mix strongly into the transition state (Figure 6a). On the other hand, when the C-H bond is weak, the base is strong (e.g., OH<sup>-</sup>) and the C-X bond is a poor acceptor, the relative magnitudes of the slopes of the curves will be reversed and the S<sub>N</sub>2-type configuration, V, will remain relatively far from the I-IV intended crossing point. As a consequence, its contribution to the transition state will be small, the interaction between B and C<sub>α</sub> will be unimportant, and the transition state will become, what is termed, an E2H type (Figure 6b).

We can now consider the major experimental evidence that questioned the existence of the E2C mechanism: the absence of a strong steric effect in E2C-type substrates. Bunnett<sup>29c</sup> has raised the valid point that if E2C substrates undergo some B---C<sub>α</sub> interaction in the transition state, then S<sub>N</sub>2 and E2C reactions should respond similarly to steric effects. In fact, this is not observed. S<sub>N</sub>2 reactions show a high sensitivity to steric bulk while E2C reactions do not. This different response to steric bulk seems to question the basic tenet of the E2C mechanism, that there exists a stabilizing interaction between the base, B, and C<sub>α</sub>.<sup>32</sup> However, if we examine the makeup of the E2C transition state (eq 14) we see that it is partly composed of the product configuration, IV, and not just I and V. Mixing in of IV, which contains no B---C<sub>α</sub> interaction, will clearly lead to a looser transition state (with regard to B---C approach) and hence to a smaller sensitivity to steric bulk. By contrast an S<sub>N</sub>2 transition state is composed of just configurations I and V and is therefore predicted to be tighter. It is not surprising, therefore, that the looser E2C transition state will show a smaller response to steric effects than the tighter S<sub>N</sub>2 transition state.

An interesting extension of the E2C mechanism is exhibited in Figure 6c. If reaction conditions are such that the S<sub>N</sub>2 configuration, V, is particularly stable, than an elimination reaction will take place via an intermediate whose main VB wave function is V (eq 15). Chemically speaking this intermediate is a radical ion which arises from the electron-transfer from the base B to the C-X moiety.<sup>33</sup>



This pathway is an extreme case of the E2C mechanism and we designate it E2C-I to denote the incursion of an intermediate preceding elimination. As far as we are aware, no evidence exists for precisely such a mechanism.<sup>34</sup> However, this mechanism completes the elimination jigsaw puzzle. The proper E2 reaction arises from the intersection of I with IV, a configuration which involves diexcitation with respect to I. On the other hand, the monoexcited configurations, II and III, may lead to eliminations

(32) An attempt to reconcile this contradiction has been provided by McLennan; see ref 22b.

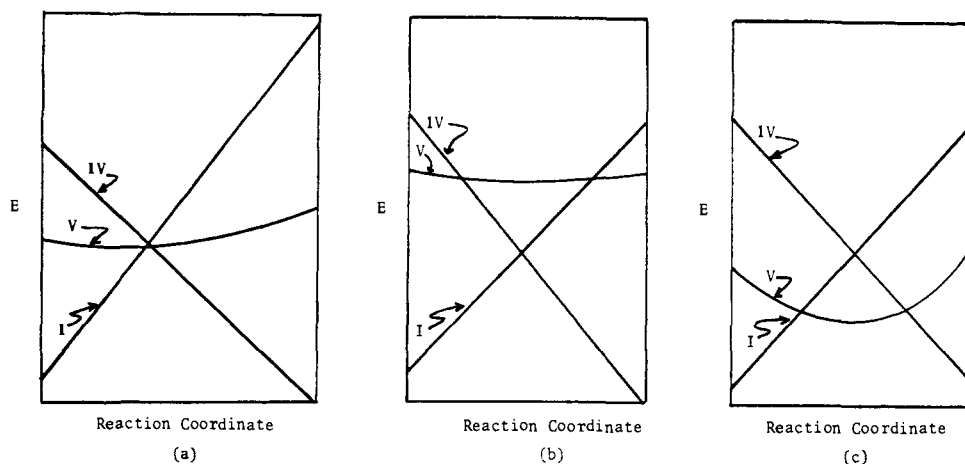
(33) The (C-X)<sup>·</sup> moiety which arises from an electron transfer from B to the C-X bond is described by the two VB components: (C·:X) + λ(C·:X). Similarly, a better description of the electron transfer from B to the C-H moiety to generate (C-H)<sup>·</sup> is (C·:H) + λ(C·:H). In our description of the configurations IV and V, we use only the main VB forms C·:X and C·:H, respectively, in accord with our simplification policy.

(34) A mechanism which appears to incorporate some of the features of the E2C-I mechanism has recently been proposed for the elimination reaction of ArCH(Cl)CMe<sub>2</sub>(NO<sub>2</sub>)<sup>-</sup> with Me<sub>2</sub>(NO<sub>2</sub>)C<sup>-</sup>.<sup>35</sup> Here the radical-anion [ArCH(Cl)CMe<sub>2</sub>(NO<sub>2</sub>)<sup>-</sup>]<sup>·</sup> was formed followed by expulsion of Cl<sup>-</sup>, and then reductive elimination to give ArCH=CMe<sub>2</sub>. This class of elimination differs from those discussed here since a proton is not one of the species eliminated from the substrate and thus this pathway does not actually compete with base-catalyzed E1cB and E2 mechanisms (though it does with the E1 pathway).

(35) Girdler, D. J.; Norris, R. K. *Tetrahedron Lett.* **1975**, 2375.

(30) See, for example, Parker, A. J.; Ruane, M.; Biale, G.; Winstein, S. *Tetrahedron Lett.* **1968**, 2113.

(31) Biale, G.; Parker, A. J.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2235.

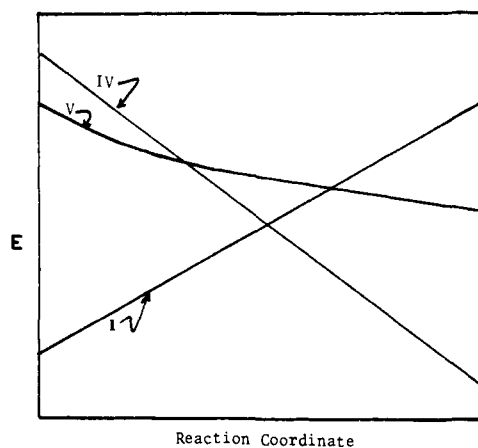


**Figure 6.** The E2H–E2C–E2C–I spectrum is shown with the aid of the VB configurations I, IV, and V. (a) A typical E2C case where I, IV, and V are close in energy at the intended crossing point in the vicinity of the transition state. (b) A typical E2H case where V is higher than I and IV in the vicinity of the transition state. (c) The case of E2C–I, where V is more stable than either I or IV in the vicinity of the transition state. The changes in the energy differences between IV and V at the reaction starting point in (a) and (b) reflect the variation in the leaving group ability of X<sup>-</sup> (i.e., the acceptor ability of the C–X bond). The relative positions of V in (a), (b), and (c) reflect the changes in the leaving group ability of X<sup>-</sup> (i.e., the acceptor ability of the C–X bond). The diagram is schematic.

via intermediates: the E1cB pathway via a carbanionic intermediate, and the E1 pathway via a carbocationic intermediate, with an entire spectrum of E1–E2–E1cB cases lying in between. The remaining monoexcited configuration, V, is responsible for the E2H–E2C spectrum. Thus the E2C–I mechanism supplies the missing link. When the S<sub>N</sub>2 configuration is sufficiently low in energy at some intermediate point along the elimination pathway, but when the S<sub>N</sub>2 pathway itself is precluded, the possibility exists that a radical-anion intermediate will be formed. This radical-anion intermediate appears to be the elimination analogue of the radical-anion intermediate observed during certain types of substitution reactions.<sup>36</sup> Clearly, if in addition to the C<sub>α</sub>–X bond, the H–C<sub>β</sub> bond is also a good electron acceptor, then the radical-anion intermediate (eq 15) will be delocalized over both C<sub>α</sub>–X and H–C<sub>β</sub> moieties.<sup>33</sup>

It is now appropriate to answer the question why elimination takes place at all if the S<sub>N</sub>2 configuration is originally lower in energy. To answer the question in general is far from trivial, since part of the elimination spectrum covers E1cB and E1 cases which also originate from monoexcited configurations (II, III). However, if we focus on the competition between proper E2 and S<sub>N</sub>2 reactions, the one factor which appears to be of overwhelming importance in governing the elimination–substitution preference is the steric congestion of the substitution pathway. Thus, merely increasing the size of the base (nucleophile) from methoxide to *tert*-butoxide leads in 2-hexyl halides to almost total elimination rather than substitution, despite the absence of significant electronic changes.<sup>37</sup> Similarly, steric congestion at C<sub>α</sub> also leads to predominant elimination.<sup>38</sup>

How can we understand the effect of steric congestion on the S<sub>N</sub>2/E2 ratio? Inspection of configuration V reveals that along the substitution pathway it undergoes stabilization owing to C<sub>α</sub>↑↓·B bond formation. When C<sub>α</sub> or B are sterically crowded the slope of descent of V will be small, and hence the barrier for substitution large. This will not be the case for configuration IV which descends steeply as B approaches the H–C<sub>β</sub> moiety and may



**Figure 7.** Energy of reactant, I, product, IV, and substitution, V, configurations for the case where the substitution pathway is sterically congested. This results in V exhibiting a small slope.

eventually intersect I to create a smaller barrier for elimination. These considerations are illustrated in Figure 7. Clearly other factors (e.g., solvent effects) are also likely to influence the elimination–substitution ratio. However, at this stage such effects cannot be predicted using the simple VB model.

**E. Concertedness of C–H and C–X Bond Cleavage.** An interesting corollary to the preceding analysis is the nature of the seemingly synchronous E2 reaction. For a bimolecular elimination reaction the synchronicity of H–C<sub>β</sub> and C<sub>α</sub>–X cleavage depends on the degree of mixing of II, IV, and V into I along the reaction coordinate (eq 13 and 14). Each configuration will endow the reaction complex with its characteristic features. Thus II prefers a loose H–C<sub>β</sub> bond and a tight C<sub>α</sub>–X bond while V prefers exactly the opposite. The product configuration, IV, prefers both H–C<sub>β</sub> and C<sub>α</sub>–X bonds to be loose.

The degree of mixing of these configurations into I depends on their relative energies. At the reaction starting point the most stable configuration of the three is V. This is because IV is a diexcited configuration, II involves an electron jump to the C–H bond, while V involves an electron jump to the C–X bond. Since for most E2 substrates the C–X bond is a better acceptor than the C–H bond,<sup>39</sup> V will initially be lower than II in energy. This

(36) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745. The systems investigated by Kornblum, e.g., nucleophilic attack on *p*-nitrobenzyl halides, have two relevant charge-transfer states, D<sup>+</sup>A<sup>-</sup>, which involve an electron jump from the nucleophile to the substrate. In the first the electron jumps to the σ\*<sub>C–X</sub> bond and in the second to π\* of the *p*-nitrophenyl system. The second state is initially lower in energy, and this is the one which gives rise to the benzyl anion radicals. The first state could in principle lead to an S<sub>N</sub>2 reaction, but since in most of the systems the benzylic carbon is substituted with many groups, nucleophilic attack is not easy.

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(39) The electron affinities (EA) of various bonds were estimated thermochemically by one of us (S.S.S.) relative to the C–I bond (for which EA = 0 by definition) to be (kcal/mol): C–H ≈ -83, C–Cl ≈ -20, C–Br ≈ -11, C–F ≈ -48.



means that in regular E2 eliminations *C-H bond cleavage may lag behind C-X cleavage*. There is abundant evidence to support this idea. As noted by McLennan,<sup>22b</sup> primary  $\beta$ -deuterium isotope effects are invariably low in unactivated systems;  $k_H/k_D$  values generally lie between 2 and 4, well under the theoretical maximum value of ca. 7 for the half-transferred proton. It is only when the C-H bond is activated (e.g., by  $\beta$ -phenyl groups) that the  $k_H/k_D$  values ( $\sim 4-6$ ) begin to approach the theoretical maximum. Activation of the C-H bond, of course, coincides with improving its electron-accepting ability so that configuration II now becomes more competitive with V. *Thus we conclude that an elimination reaction in which the C-H and C-X bonds undergo similar degrees of bond-breaking in the transition state really involves substantial E1cB character*. This conclusion marks a significant departure from views based on the potential energy surface models.

The question of syn vs. anti elimination now takes on additional clarity and lends support to ideas recently proposed by Bach et al.<sup>40</sup> It is experimentally well established that E2 eliminations prefer the anti periplanar configuration, and that as the carbanionic character of the transition state increases the preference for *syn* elimination increases also.<sup>22</sup> If the key configurations in the transition state are IV and V (i.e., involve an electron jump to the C-X bond), then base attack will be anti since the electron jump is best facilitated by backside attack, in analogy to the  $S_N2$  reaction.<sup>40</sup> As the importance of the carbanionic configuration, II, increases (i.e., increased electron jump to the C-H bond), the stereospecificity of base approach, vis-à-vis the leaving group, will *decrease* facilitating *syn* elimination. Thus the present analysis conforms entirely with the observation that *syn* coplanar E2 elimination involves a considerable amount of carbanionic character in the transition state.

### Conclusions

The present paper has attempted to generate a simple qualitative model for analyzing problems of reactivity in organic chemistry. We must point out quite clearly, however, that a model, whose

basic tool is Lewis-type structures, cannot attempt to explain all subtle aspects of chemical reactivity. This has not been our goal. The model is meant to provide a conceptual framework for "thinking" about organic chemistry—a model which is based on sound quantum mechanical principles and, despite its simplicity, appears capable of tackling a complex organic reaction and rationalizing many of its features.

Many of the conclusions concerning elimination reactions which were reached in this paper are in accord with current thinking. The major difference is that it demonstrates in a methodical manner: how does the reaction barrier arise; when does the transition state acquire, for example, carbanionic character; and how might the spectrum of reaction types ultimately generate a bona fide intermediate?

Regarding the E2C-E2H spectrum, a subject which remains somewhat controversial, the VB model provides a sound basis for understanding the experimental findings. Thus the anomalous result that increasing the steric bulk of the substrate in  $S_N2$  reactions reduces the  $S_N2$  rate but has little effect on the E2 rate does indeed appear to be due to a looser transition state (with regard to the B---C $_{\alpha}$  distance) in elimination reactions.

We conclude, therefore, that despite the simplicity of the model, its quantum mechanical foundation and "chemical" form may lead to an intuitive tool for both understanding and predicting aspects of chemical reactivity. In future papers we hope to apply this model in conjunction with the D-A format and thereby to generate reliable predictors of reactivity, such as the initial energy gap of the intersecting configuration and their mutual slopes, which, together, dominate the barrier height. Some progress along this line has been made by us for the  $S_N2$  reaction.<sup>41</sup>

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