this reaction pathway is at best only minor, a more circuitous argument can be constructed which otherwise defines the stereochemistry of the hydroxyl bearing carbon in **13**.

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A Theory of Free Radical Reactions

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Abstract: The simple three-center three-electron model introduced by Yamaguchi is used to describe the elementary abstraction–addition step in the approach of a free radical to a bonded pair of atoms. Consideration of all *covalent* resonance structures shows the colinear approach to be "exchange allowed" and the equilateral triangular approach to be "exchange forbidden". Inclusion of all *polar* resonance structures, as a perturbation to the previous situation, shows that addition of a free radical to a double bond tends to occur at that position for which the incipient bond has maximum partial ionic character. If the position of attack is also that favored from thermodynamic considerations, ionic effects will simply reinforce the thermodynamic control. If the position of attack is opposite to that for the more stable product, ionic and thermochemical controls will compete, with the possibility of contrathermodynamic orientation of addition. These two cases are illustrated by ab initio calculations on simple $Cl\cdot + XHC{=}CH_2$ addition reactions.

Introduction

Free-radical reactions are extremely versatile.[2] The great variety of reactions seem to occur, however, through a limited number of *elementary steps*. For reaction with closed-shell molecules, the two most common elementary steps are *abstraction* of hydrogen atoms from RH bonds[3a] and *addition* to saturated centers.[3b,c] A third, less common elementary step is S_H2 type substitution.[4] The other substitution reactions involve either an abstraction step as in allylic substitution, or an addition step, as in aromatic substitution. Carbenes, of course, will insert into bonds, but generally as singlets with two paired electrons; as such the insertion reaction is not a free-radical reaction proper. Triplets may also insert, but again via multiple steps. With other radicals, reactions such as dimerization and disproportionation may take place. In analogy with photochemical reactions, free-radical reactions can be tailored to yield products which would be difficult to obtain by thermal reactions involving intangible electron pairs.[5] A long-standing topic of interest has been the role of "polar effects" in determining the structure and energy of free-radical reaction transition states.[6] A particularly important question is the extent to which these polar effects may eventually be involved in the *orientation* of free-radical additions, in competition with the relative thermodynamic stabilities of possible primary products.[3b,c,7]

Theoretical attempts at describing free-radical reactions can be traced back to the early days of quantum chemistry. The three-center three-electron system H_3 was one of the first systems to be studied by the traditional valence-bond method.[8] At that time the aim was a quantitative description of the potential energy surface for a chemical reaction. More recently three-electron systems have been considered by Matsen, using a spin-free approach which is closely related to the valence-bond method.[9] Various calculations have recently been performed on specific radical reactions.[10] These theoretical studies have been carried out in the same context as studies of the reactions of closed-shell systems; similar orbital interactions are

invoked. Recently, Yamaguchi has made the first attempt to rationalize the behavior of free-radical reagents on the basis of a model which incorporates explicitly the essential characteristic property of these reagents—an unpaired spin.[11] He considered a set of three-electron spins, two of which are initially paired, while the third one seeks out a partner spin from this initial pair. Using a phenomenological Heisenberg Hamiltonian, equivalent to a simplified valence-bond approach in which electron exchange alone is included, Yamaguchi obtained correlation diagrams for the doublet states and the quartet state. These correlation diagrams show qualitatively different behavior for the linear configuration (which was identified with the abstraction process) and for the triangular configuration.[12] In analogy to the Woodward–Hoffmann rules, Yamaguchi concluded that the linear approach is "spin-symmetry allowed" with no crossing between the two doublets, while the triangular approach is "spin-symmetry forbidden" with crossing doublets (compare also ref 8a). This last result is particularly surprising, in view of the extremely facile addition of halogen atoms to double bonds.[12]

In the present work we reconsider the three-center three-electron model for the elementary abstraction–addition reaction step. The energies of the different states for a purely covalent model are then obtained in a straightforward manner from the exact three-particle Hamiltonian. We draw out correlation diagrams for different orientations of approach of the free-radical reagent to the bond. We next extend the simple model, based on covalent structures, to include ionic structures. It is possible to discuss the effect of ionic character in the incipient bond in a qualitative manner. Our main results are: (1) For purely covalent interactions the colinear end-on approach has a small activation barrier ("exchange allowed"), while the triangular approach is favorable only if the free radical can maintain zero overlap with one of the centers of the initial bond. Otherwise the triangular approach is "exchange forbidden". These results are specific to the three-electron model and do not appear in the one-electron approach commonly used for even-electron systems. (2) When ionic interactions are

important, addition of a free radical to a bond substituted by a donor or acceptor substituent tends to occur at that position for which the incipient bond of the transition complex has the biggest possible partial ionic character.

Three-Center Three-Electron Model for the Elementary Abstraction–Addition Step

We can illustrate the abstraction process in Scheme I. In (1)

Scheme I

(1)   (2)   (3)
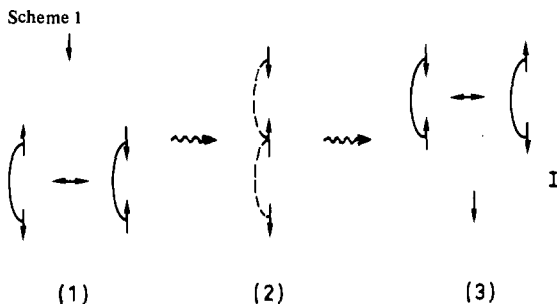
an odd electron spin approaches an electron pair which is described by resonance between two bonded structures, in which the two electrons are respectively (up, down) or (down, up). Situation (2) describes the transition state, in which the incoming electron has "selected" the resonance structure with appropriate opposite spin on the nearest center. Finally, in (3), the new bond is totally formed; concurrently the bonded spins can either be (up, down) or (down, up)—while the third electron is now isolated.

The addition process can be illustrated in a *quasi-identical fashion*.[13] The single difference is the existence of an additional, σ, bond between the two initially paired electrons. Hence they stay attached, and the third electron can only bond to one end (Scheme II). The two schemes are valid whatever the

Scheme II

(1)   (2)   (3)
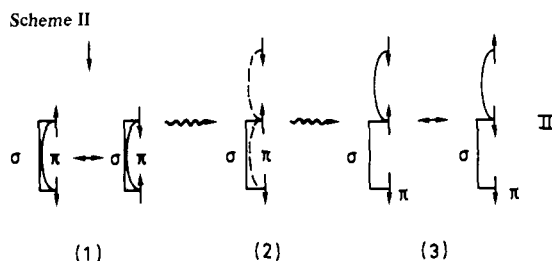
relative orientation of the initial bond and of the direction of the attacking radical. *Thus in the three-electron model the orientation of attack can in no manner distinguish a priori between abstraction or addition.* Of course addition cannot occur by attack rigorously *in* the olefinic plane and will be more likely in a direction perpendicular to the plane of the double bond. But a nearly end-on attack is entirely feasible:
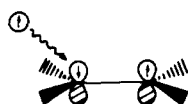
This is the favored orientation for nucleophilic addition reactions[14] where the dominant interaction is that between substrate and π^* orbital and is probably also favorable for addition of nucleophilic radicals.

A model which incorporates the essential features of Schemes I and II, and which also allows for ionic pairing of the electrons, is constituted by three centers in which we can arbitrarily distribute the three electrons:
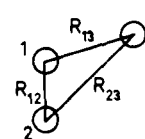
The electrons can occupy any center, either alone *or* with a partner with antiparallel spin. Such a distribution allows for two doublet states and one quartet state.[15] In the following we will concentrate on the two doublet states. We are aware, however, that—just as in thermal reactions of closed-shell systems, involving singlet diradicals, a transient triplet diradical *may* sometimes be involved[16]—*during the reaction process the quartet state may be formed in a transient manner.*

Purely Covalent Model

We first consider all covalent resonance structures for the three-spin system. There are three of these:

a   b   c
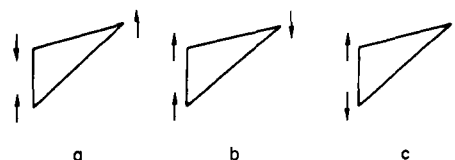
Each one of these structures can be described by a single Slater determinant of localized spin orbitals. For instance the determinant representing the first resonance structure is

$$D^1_{23} = |\phi_2 \alpha \phi_3 \alpha \phi_1 \beta|\tag{1}$$

where ϕ_1, ϕ_2, and ϕ_3 are undefined spatial wave functions for the three centers. The lower subscripts on D indicate the presence of α spins and the higher subscript a β spin.

The exact Hamiltonian is introduced in the usual form

$$\mathcal{H} = \sum_i h(i) + \sum_{i<j} \left(g(ij) + \frac{Z_i Z_j}{R_{ij}} \right)\tag{2}$$

where i and j run from 1 to 3, and h and g are the familiar one-electron and two-electron operators. The last term represents the nuclear–nuclear repulsion; R_{ij} is the distance between centers i and j. From (1) and (2), it is straightforward matter to write out the secular determinant of the problem. After elimination of the quadruplet, the secular determinant for the doublet wave functions

$$^2\psi_1 = \frac{1}{\sqrt{2}} [D^1_{23} + D^2_{13}]$$

$$^2\psi_2 = \frac{1}{\sqrt{6}} [2D^3_{12} - D^1_{23} + D^2_{13}]\tag{3}$$

takes the form

$$\begin{vmatrix} A - \mathcal{J} + J_{12} - \frac{1}{2}(J_{23} + J_{13}) - E(1 - \mathcal{S} + \sigma_1) & \frac{\sqrt{3}}{2}(J_{23} - J_{13}) - E\sigma_2 \\ \frac{\sqrt{3}}{2}(J_{23} - J_{13}) - E\sigma_2 & A - \mathcal{J} - J_{12} + \frac{1}{2}(J_{23} + J_{13}) - E(1 - \mathcal{S} - \sigma_1) \end{vmatrix} = 0\tag{4}$$

where

$$A = \sum_i h_{ii} + \sum_{i<j} \left[(ii|jj) + \frac{Z_i Z_j}{R_{ij}} \right]$$

$$J_{ij} = S_{ij}[2h_{ij} + S_{ij}h_{kk} + 2(ij|kk)] + (ij|ji)\tag{5}$$

$$\mathcal{J} = h_{ij}S_{ik}S_{kj} + S_{kj}(ki|ij) + \text{circular permutations}$$

$$\mathcal{S} = S_{12}S_{23}S_{31}$$

$$\sigma_1 = \frac{1}{2}(2S^2_{12} - S^2_{23} - S^2_{13}) \quad \sigma_2 = S^2_{23} - S^2_{13}$$

In eq 5 S_{ij} is the overlap between the two centers i and j and the matrix elements of h and g are described in the usual
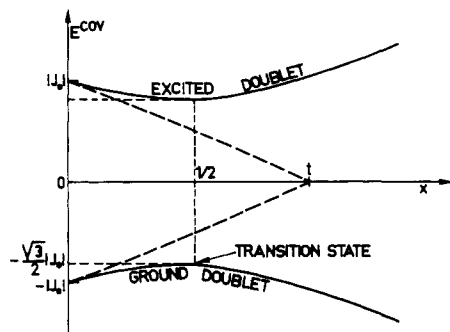
Figure 1. Energies of the two doublet states for the colinear approach. The quantity $A - \mathcal{J}$ is chosen as zero of energy. This figure also applies to the triangular approach in which zero overlap is maintained with one center.

notation; $h_{ij} = \langle i|h|j\rangle$. $(ij|kl) = \langle i(1)j(1)|g|k(2)l(2)\rangle$. The valence-bond exchange integral J_{ij} is usually a negative quantity.[17]

The doublet $^2\psi_1$ (eq 3) can be interpreted in the VB sense as the resonance structure with the bond localized between centers 1-2 ($|\cdot$). The other doublet $^2\psi_2$ (eq 3) describes the linear combination of structures with bonds between 1-3 and 2-3 ($\cdot\backslash$ and $\cdot/$), respectively.

The diagonal elements of eq 4, which represent the energies of the VB structures, can be obtained directly according to classical rules.[8b,c] In the traditional valence-bond manner we neglect $\mathcal{S}$ in comparison with $\mathcal{J}$ and S_{ij}^2 in comparison with J_{ij}. The roots of determinant 4 for two doublets are then given by

$$E_{\mathrm{I,II}}^{\mathrm{COV}} = A - \mathcal{J} \pm \left\{\frac{1}{2}\left[(J_{12} - J_{13})^2 + (J_{12} - J_{23})^2 \right.\right.$$
$$\left.\left. + (J_{13} - J_{23})^2\right]\right\}^{1/2} \quad (6)$$

We shall use eq 6 to study different orientations of approach of a center 3, assumed initially at infinity, to a pair of centers 1 and 2, assumed to be initially bonded. Equation 6 for this purpose can be written as:

$$E_{\mathrm{I,II}}^{\mathrm{COV}} = A - \mathcal{J} \pm \frac{|J_{12}|}{\sqrt{2}}\sqrt{(1 - x)^2 + (1 - y)^2 + (x - y)^2}$$
$$= A - \mathcal{J} \pm \epsilon \quad (7)$$

where the variables x and y are defined as

$$x = J_{13}/J_{12}$$
$$y = J_{23}/J_{12} \quad (8)$$

Therefore, the essential variables are the distances R_{13} and R_{23} which will be reflected respectively in J_{13} and J_{23}. The integral
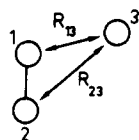
J_{12} is assumed to be a constant J_0. This is perfectly reasonable for addition. For abstraction the 1,2 bond length must ultimately stretch, so that the assumption is valid only in the initial stages of the attack. The quantity ϵ in eq 7 describes the characteristic bonding properties of the system. Therefore, the term $A - \mathcal{J}$ is not considered in the qualitative discussion of the correlation diagrams, even when its distance dependence is in general not negligible.

A. Colinear End-On Approach. Since R_{23} is significantly larger than R_{13}, except at very large distances, y can be ne-

glected relative to x *except for very small x*. The energies of the two states are plotted in Figure 1, as a function of increasing x, i.e., decreasing distance R_{13}.

At infinity, the two doublet states have energies $-|J_0|$ and $|J_0|$. This corresponds to an atom 3 at infinite distance from a molecular singlet or a molecular triplet (in the latter case, the odd spin is opposite to the overall triplet spin). As the atom starts approaching, i.e., at large distances, $y \approx x$ and the energies behave as $\pm|J_0|(1 - x)$. The energy of the ground doublet state rises and then rapidly curves off, since at $x = 1$, the energy is again $-|J_0|$.

The transition state occurs for $x = \frac{1}{2}$ (assuming now $y = 0$), and the barrier is

$$\Delta E = |J_0|\left(1 - \frac{\sqrt{3}}{2}\right) \quad (9)$$

We can estimate ΔE for (a) addition to an olefin; (b) abstraction of a hydrogen atom from a CH bond.[18] We have just seen that in our model the triplet-singlet separation in the 12 bond is equal to $2|J_0|$. In ethylene the $^3\pi,\pi^*$ state lies at ~ 4 eV,[19] while in saturated hydrocarbons the lowest $^3\sigma,\sigma^*$ state lies around 10 eV.[20] Hence the activation energies are ΔE (addition) ≈ 6 kcal/mol and ΔE (abstraction) ≈ 15 kcal/mol.

These numbers are remarkably reasonable in view of the simplicity of the model. The location $x = \frac{1}{2}$ of the colinear approach indicates a relatively loose transition state.

The possibility of existence of a small barrier in the colinear approach is not revealed in Yamaguchi's paper,[11a] due to the approximations involved in the Heisenberg Hamiltonian.

B. Perpendicular Approach. We consider now the approach of radical 3 perpendicular to the bond 1-2. Two cases of interest are $J_{31} = J_{32}$, corresponding to an approach toward the center of bond 1-2 (isosceles triangle) and $J_{31} \neq 0, J_{32} \approx 0 \gg J_{31}$ corresponding to a configuration in which orbitals centered on 3 and 2 are *orthogonal*, for instance the rectangular trian-

$$J_{13} = J_{32} \qquad\qquad J_{32} \approx 0 \gg J_{31}$$

gular approach shown on the right-hand side (cf. ref 21). These two cases correspond respectively to $y = x$ and $y = 0$. From eq 7 we then obtain immediately:

(isosceles triangle) $E_{\mathrm{I,II}}^{\mathrm{COV}} = A - \mathcal{J} \mp |J_0|(1 - x)$ (10a)

(one zero overlap) $E_{\mathrm{I,II}}^{\mathrm{COV}} = A - \mathcal{J} \mp |J_0|\sqrt{1 - x + x^2}$

(10b)

The corresponding energies are shown in Figure 2 for the isosceles triangle. For the zero-overlap case, the result is essentially identical with Figure 1 for the linear approach, *with only a small activation energy*.

A surface crossing occurs for the equilateral triangular configuration ($x = 1$), which has D_{3h} symmetry in our model where all the localized orbitals are of the same type. There is a Jahn-Teller degeneracy between the two $^2E'$ states. The large barrier $\Delta E = |J_0|$ along the lower surface makes such a reaction highly improbable. Although in certain cases the term $A - \mathcal{J}$ may wash out at least part of the barrier, qualitatively the reaction is "forbidden". Therefore, it appears that an approach perpendicular to the middle of the bond will be favorable only if the free radical can maintain *zero overlap* with one of the bond termini. The crossing of two doublet states for the equilateral triangle ($x = 1$) is in agreement with Yamaguchi's
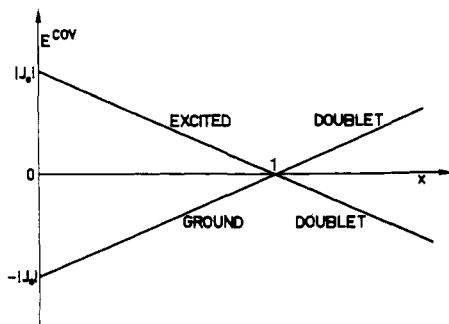
Figure 2. Energies of the two doublet states for the triangular approach $(J_{13} = J_{32})$. The quantity $A - \mathcal{J}$ is chosen as zero of energy.
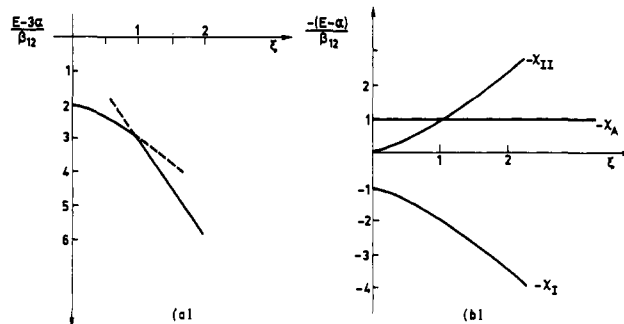

Figure 3. (a) Energy of the ground-state doublet for the isosceles approach of center 3 to bond 1-2. Second doublet in the neighborhood of crossing is given by the broken line. (b) The corresponding MO energies. $\chi = (E - \alpha)/\beta_{12}$ (χ_A: antisymmetrical MO; χ_I and χ_{II}, the two symmetrical MO's).

earlier result,[11] but his model does not yield explicitly the barrier.

It is interesting to note that *mathematically* for $y = -x$, i.e., $J_{32} = -J_{31}$, or for $y = x < 0$, i.e., $J_{32} = J_{31} > 0$, eq 7 yields no barrier in the ground doublet. By definition in valence-bond theory exchange integrals are approximately proportional to the *square* of the overlap and in the normal chemical case are negative. Only for ferromagnetic materials is it assumed that J_{ij} can be a positive quantity. Hence these two mathematical solutions do not seem to correspond to any real situation in gas-phase or solution chemistry.

C. The Hückel Approximation for a Three-Center Three-Electron System. Because the valence-bond and simple molecular orbital approximations represent opposite extremes in the treatment of electron correlation, and since a realistic description lies in between, we recall the Hückel scheme for a three-electron three-center system. The total Hückel state energy for the isosceles approach of a center 3 to a bond 1-2 is:

$$E = 3\alpha + \frac{\beta_{12}}{2}(3 + \sqrt{1 + 8\xi^2}) \quad \text{for } \xi \leq 1$$
$$E = 3\alpha + \beta_{12}\sqrt{1 + 8\xi^2} \quad \text{for } \xi \geq 1$$
(11)

where $\xi = \beta_{23}/\beta_{12} = \beta_{13}/\beta_{12}$ (Figure 3a). The energy is a decreasing function of ξ and has a discontinuous first derivative at $\xi = 1$ corresponding to the crossing of symmetrical and antisymmetrical MO's (Figure 3b).[22] In contrast to the ordinary valence-bond model and to our slightly more general model, the Hückel approximation does not give rise to any energy barrier (compare Figures 2 and 3a).

The Hückel energy for the colinear approach of the center 3 to the bond 1-2 decreases continuously from the value $E = 3\alpha + 2\beta_{12}$, again in contrast with the results of the previous model. For an equidistant linear array $(\beta_{12} = \beta_{23})$ the Hückel energy $E = 3\alpha + 2\sqrt{2}\beta_{12}$ is still higher than for the equilateral triangle $(E = 3\alpha + 3\beta_{12})$, a result which is contradicted by the previous calculations.

D. Physical Interpretation of the Directivity of Preferred Approach, Comparison with Even-Center Even-Electron Systems. We have shown that the colinear approach of an odd radical to a bond is "exchange allowed" with a weak barrier, while the triangular approach is "exchange forbidden" except for the specific case of zero overlap between two of the centers. We now seek an interpretation of these results, the important part of which figure in Yamaguchi's paper,[11] as well as in implicit form in London's pioneering work[8a] in the late 20's.

The energy of a valence-bond structure with $2n$ electrons and n bonds in a cyclic array is higher than the valence-bond energy of n bonds among which no electron exchange can take place. Of course, the energy of the cyclic system is lowered by the interaction among all valence-bond structures which can be drawn for such a system (the so-called resonance energy). This energetic feature of simple valence-bond theory does not

show any specific difference between $4n$ and $(4n + 2)$ cyclic systems. Only in higher approximations does the valence-bond method distinguish between $4n$ and $(4n + 2)$ cyclic systems, and Hückel from Mobius arrays.[23] The features of four-center four-electron system relevant for comparison with odd-electron systems are reviewed in the Appendix.

For three-electron three-center systems the lowering of energy by resonance among the valence-bond structures is much more sensitive to the actual geometry of the system. The equilateral triangle geometry is an extreme case for which there is no resonance energy at all, because the doublets are two orthogonal components of the degenerate symmetry representation. This is mathematically expressed by the zero values of the off-diagonal elements of the determinant 4 for the equilateral geometry. On the contrary, the two doublets for a colinear array do not belong to the same irreducible representation of the symmetry group, and they can therefore interact, giving rise to a resonance energy. Consequently, the energy of a colinear array is lower than the energy of an equilateral triangle. The main distinction between the two geometries is therefore one of *like* or *unlike* symmetry of the two interacting ("resonating") doublet components which contribute to the ground electronic state. A possible simple interpretation is the rationale first proposed by Herschbach.[24] An electron ($\uparrow$) approaching the middle of a bond automatically finds *one* of the two paired spins ($\uparrow\downarrow$) at the bond termini with the *wrong* orientation for incipient bonding. On the other hand, an electron ($\uparrow$) approaching a bond end-on can always select, amongst the two equally probable ($\uparrow\downarrow$, $\downarrow\uparrow$) pairing situations in the bond, *that* which provides its nearest partner with the *correct* orientation for incipient bonding. An equivalent interpretation is based on the violation of the "valence saturation principle"[8a] for *all* atoms in the triangle, but for only *one* atom in the linear array. For odd-electron systems the pairing properties describing "valence saturation" are mirrored in the resonance energy which varies within a large interval and can even vanish. A strikingly different situation holds for even-electron systems, for which the resonance energy varies within a much smaller interval, because pairing among even numbers of electrons is always present to some extent, due to delocalization. In summary, although the valence-bond method is not sensitive enough to characterize the important specific delocalization properties of even-electron systems, which are better described by the simplest one-electron approximation (Woodward-Hoffmann rules), it describes "valence saturation", and therefore the directional properties of free-radical reactions, better than the one-electron approximation.

These simple qualitative considerations are in good agreement with the well-known preferred *colinear* reaction path for the $H + H_2$ reaction, while throwing new light on its mecha-

nism. For this reaction, which is formally equivalent to the abstraction of one of the bound H atoms by the external H atom, recent ab initio calculations with inclusion of correlation[25] confirm the colinear geometry first demonstrated by valence-bond methods.[8a] In the reactive scattering of deuterium atoms by Cl_2, the colinear reaction geometry is also preferred.[24b,26] Other recent experimental evidence also seems to provide support for the theoretical result. In the intramolecular displacement reaction of **1** only the *colinear* (C_1SR') abstraction of sulfur occurs, to yield **2**, while the *triangular* (C_1SC_2) abstraction of carbon, to yield **3**, is not observed.[27]
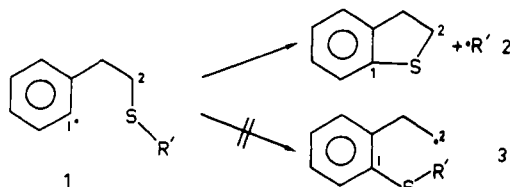
Inclusion of Ionic Structures

The previous model is readily extended to study polar effects by including the six polar structures corresponding to a negative charge on one center, a positive charge on the second center and an odd electron on the third center. The role of such ionic resonance structures in stabilizing the transition state for free-radical reactions was first suggested by Walling.[6a] Again each of these structures can be described by a single Slater
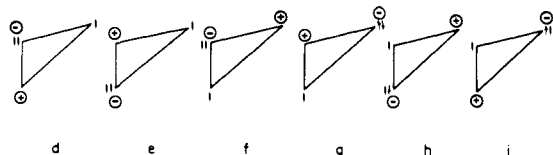
determinant, which we will denote by D_{ij}^i, for the structure with two electrons on center i and one electron with α spin on center j. The secular determinant for the simultaneous treatment of all nine structures becomes more complicated, since it would correspond, in molecular orbital language, to a full configuration interaction calculation.

At the outset we simplify the problem by introducing the zero-differential-overlap approximation for the matrix elements between polar and covalent structures and among the polar structures themselves. We then expand the secular determinant by using the purely covalent 2-by-2 block as zeroth order term, and by including the effect of the polar structures to second order in the interaction between polar and covalent structures. This is justified since the polar wave functions lie much higher in energy than the covalent ones. The total energy of the two doublet states is given by

$$E_{\mathrm{I,II}}^{\mathrm{COV+IONIC}} = E_{\mathrm{I,II}}^{\mathrm{COV}} - \sum_{i<j=1}^{3} \left[\frac{\gamma_{ij}^2}{\alpha_{ij} \mp \epsilon} + \frac{\gamma_{ji}^2}{\alpha_{ji} \mp \epsilon} \right]$$
$$\times \left[1 \pm \sum_{k<l=1}^{3} (J_{kl} - 3J_{ij})/2\epsilon \right] \quad (12)$$

where $E_{\mathrm{I,II}}^{\mathrm{COV}}$ and ϵ have been taken from eq 7. The choice of sign in the two brackets discriminates between the two doublets. The quantity $\gamma_{ik} = \langle D_{ij}^k|H|D_{ij}^i \rangle$ describes the interaction between covalent structure D_{ij}^k and the ionic structure which is obtained by electron transfer from kth center to ith center. Note that $\gamma_{ik} = \gamma_{ki}$ only if the centers i and k are equivalent. Similarily $\alpha_{ik} = \langle D_{ij}^i|H|D_{ij}^i \rangle$ is the energy of ionic structure with two electrons at the center i and no electron at the center k.

We consider again the two cases

$$J_{13} = J_{23} \quad (y = x)$$

corresponding to the isosceles triangular approach (compare eq 10a) and

$$J_{23} \approx 0 \quad (y = 0)$$

corresponding both to the colinear attack and to the single-zero-overlap attack (compare eq 10b). Equation 12 then yields in a straightforward manner the two doublet roots for the first case: $(y = x)$

$$E_I = A - \mathcal{J} - |J_0|(1 - x)$$
$$- 2\left[\frac{\gamma_{12}^2}{\alpha_{12}} + \frac{\gamma_{21}^2}{\alpha_{21}} \right] - \left[\frac{\gamma_{13}^2}{\alpha_{13}} + \frac{\gamma_{31}^2}{\alpha_{31}} \right]$$

$$E_{II} = A - \mathcal{J} + |J_0|(1 - x) - 3\left[\frac{\gamma_{13}^2}{\alpha_{13}} + \frac{\gamma_{31}^2}{\alpha_{31}} \right] \quad (13)$$

and for the second case: $(y = 0)$

$$E_{I,II} = A - \mathcal{J} \mp |J_0| \sqrt{1 + x^2 - x}$$
$$- \left[\frac{\gamma_{12}^2}{\alpha_{12}} + \frac{\gamma_{21}^2}{\alpha_{21}} \right] \left[1 \mp \frac{x - 2}{2\sqrt{1 + x^2 - x}} \right]$$
$$- \left[\frac{\gamma_{23}^2}{\alpha_{23}} + \frac{\gamma_{32}^2}{\alpha_{32}} \right] \left[1 \mp \frac{1 - 2x}{2\sqrt{1 + x^2 - x}} \right] \quad (14)$$

assuming that $\alpha_{ij} \mp \epsilon \approx \alpha_{ij}$.

In the isosceles triangular case the doublet-state energies still cross, but their intersection occurs at a lower energy. Although the starting energies are also lowered, overall the barrier is now

$$\Delta E = |J_0| - \left(\frac{\gamma_{12}^2}{\alpha_{12}} + \frac{\gamma_{21}^2}{\alpha_{21}} \right) \quad (15)$$

which is illustrated in Figure 4. The barrier is lowered relative to its value $|J_0|$ in the covalent case (compare with Figure 2). For the colinear and the single-zero-overlap attack, the polar structures also lower the barrier, which was already quite small (see eq 9):

$$\Delta E = \left(1 - \frac{\sqrt{3}}{2} \right) |J_0| - \left(\frac{\gamma_{13}^2}{\alpha_{13}} + \frac{\gamma_{31}^2}{\alpha_{31}} \right) \quad (16)$$
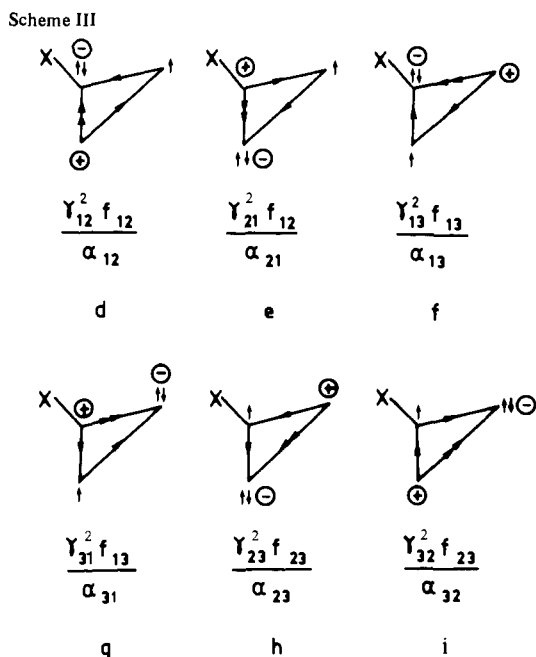
Hence, ionic terms have the general effect of decreasing the barrier.

Effect of a Donor or Acceptor Substituent on Center 1: Orientation of Free-Radical Addition

The influence of a polar substituent at one end of the bond which is attacked by a free radical can be directly studied by the proper selection of polar structures from all six possible ones. For this purpose it is also necessary to take into account the electronegativity of the attacking radical relative to both centers of the substrate bond. Let us draw six polar structures with the substituent X at center 1 and with arrows indicating charge shift among three explicitly considered orbitals from the more positive to the more negative end (+ toward − is connected with two arrows, + toward neutral, or neutral toward −, is connected with a single arrow) (Scheme III). The contribution of an individual polar structure to the perturbation eansion for the energy of the lowest doublet in eq 12 is written under the corresponding structure, with

$$f_{ij} = 1 - \sum_{k<l=1}^{3} (J_{kl} - 3J_{ij})/2\epsilon$$

Let center 1 be substituted by a donor—or acceptor—predominant group[28] which *polarizes* the double bond. A π donor (CH_3, NH_2) will stabilize an adjacent positive charge on $C(1)$ while a π acceptor (BH_2, CN) will stabilize an adjacent negative charge. Inductive effects are not explicitly considered. Let us first assume that *the electronegativity of centers 1 and*

Scheme III

$$\frac{\Upsilon_{12}^2\, f_{12}}{\alpha_{12}} \qquad \frac{\Upsilon_{21}^2\, f_{12}}{\alpha_{21}} \qquad \frac{\Upsilon_{13}^2\, f_{13}}{\alpha_{13}}$$

d   e   f

$$\frac{\Upsilon_{31}^2\, f_{13}}{\alpha_{31}} \qquad \frac{\Upsilon_{23}^2\, f_{23}}{\alpha_{23}} \qquad \frac{\Upsilon_{32}^2\, f_{23}}{\alpha_{32}}$$

g   h   i

Figure 4. Energies of the two doublet states for the triangular approach ($J_{13} = J_{32}$) when ionic structures are included. The quantity $A - J$ is chosen as zero of energy.

2 and of the radical center 3 are similar. We can characterize the net charge (δ^+ or δ^-) induced by X on 1 and 2 and the intrinsic polarities of the substrate bond 12 and of the incipient bonds schematically.

(X =donor)   (X = acceptor)
III   IV
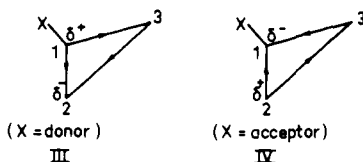
Comparison of these schemes with the available polar structures enables us to select which of these polar structures can contribute most to the overall "resonance energy". Both the net charge on atom 1 and the bond polarities are used in making this comparison. For donor substitution the sequence of polar structures which stabilize most the covalent doublet is: (III) e > g,h > other polar structures. For acceptor substitution on center 1 the corresponding sequence will be: (IV) d > f,i > other polar structures. Let us assume that the quantities $\gamma_{12}^2 f_{12}/\alpha_{12}$ or $\gamma_{21}^2 f_{12}/\alpha_{21}$ assigned to the initial bond 1–2 (and which are introduced by structures d and e) change considerably less, as the free radical approaches, than the corresponding quantities describing the incipient bond. Then, that course of free-radical attack will be favored which maximizes sufficiently the distance-dependent contributions of structures g and h in one case, f and i in the other. For both donor and acceptor substitution one structure introduces $\gamma_{13}^2 f_{13}/\alpha_{13}$, the other $\gamma_{32}^2 f_{23}/\alpha_{32}$. Hence, the conjecture can be made that, if the attacking radical has approximately the same electronegativity as the carbon termini of the double bond, ionic character will not discriminate between bonding at the substituted position and bonding at the unsubstituted position. Most likely the preferred pathway will be thermodynamically controlled.

We consider now the case where the *electronegativity of the attacking radical is substantially different from the electronegativity of both centers forming the initial bond*—as for a chlorine atom attacking a double bond. For such a highly electronegative reagent, the previous schemes must be modified as shown in Scheme IV. Both incipient bonds are polarized toward the reagent (as the latter builds up charge), but one more than the other. The electronegative reagent can accept more charge—and hence form a more polar bond—from the initially electron-rich center. The substrate bond, which was
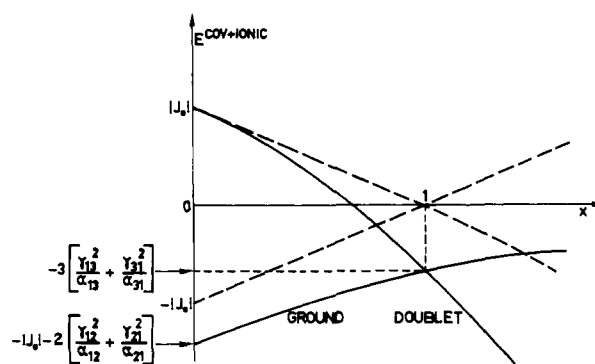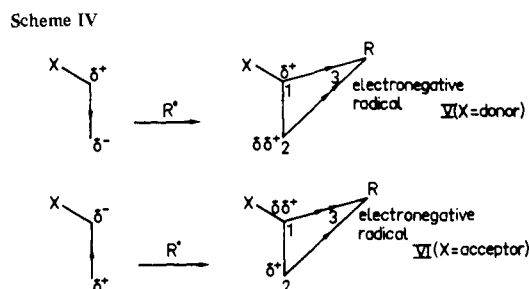
initially polar (from δ^+ to δ^-, single arrow), loses a good part of its polarity in the transition state (from δ^+ and $\delta\delta^+$, no arrow) as the electron-rich center is depleted.

Scheme IV

electronegative radical $V(X=donor)$

electronegative radical $VI(X=acceptor)$

It is clear that the reaction process V requires increasing admixture of the polar structure i, while process VI requires increasing admixture of the polar structure g. The predominance, for instance of i in V, stems both from the absolute and relative polarity of bonds 23 and 13 in V, but also from the *change in polarity* in the substrate bond 12 which is occurring in the direction indicated in structure i. This is true even though the overall polarity of bond 12 is not reversed. In structure i the distance-dependent term is $\gamma_{32}^2 f_{23}/\alpha_{32}$, while in structure g it is $\gamma_{31}^2 f_{13}/\alpha_{31}$. Hence ionic character favors free-radical attack of an electronegative reagent at the unsubstituted end of the substrate bond for process V (donor substituent) and at the *substituted* end for process VI (acceptor substituent). In VI this effect must be balanced *against* the thermochemical preference for the alternative pathway, assumed till now to be the exclusive controlling factor.[29] For an electropositive reagent, the result would be reversed, with attack at the substituted position if X is a donor, at the unsubstituted position if X is an acceptor.

Altogether the following general rule can be formulated. *All other things being equal, addition of a free radical to a double bond tends to occur at that position for which the incipient bond has maximum partial ionic character.* In particular: (1) a reagent with neither strongly electronegative nor strongly electropositive character ($H\cdot$, $CH_3\cdot$) should give the thermodynamically favored product; if the substituent stabilizes the radical site, this corresponds to attack at the *unsubstituted* position; (2) an *electronegative* radical ($Cl\cdot$, $Br\cdot$) should add initially at the negative end of a polarized double bond, an electropositive radical at the positive end. If the position of attack is also that favored from thermodynamic considerations, ionic effects will simply *reinforce* the thermodynamic control observed for electroneutral reagents. If the position of attack is opposite to that for the more stable product, the ionic stabilization of one route, and the thermochemical stabilization

of the other, will compete, with the possibility of *contrathermodynamic orientation* of the addition.

Some care must be exercised when applying these rules because of the simple nature of our model. For instance, when considering the polarization of the double bond it seems reasonable to choose the polarization of the two π electrons, because (a) the model includes only two substrate electrons and does not account for σ-core polarization; (b) the transition state for addition is certainly very loose, in a region where the odd orbital of reactant overlaps only weakly with the outer π lobes of the double bond. The polarization of the π electrons need not be in the same direction as the overall polarization of the bond (see, further, the case of cyanoethylene).

Ab Initio Calculations for Free-Radical Addition to Substituted Double Bonds

Since the essential purpose of this article is to lay out the foundations of a theory of free-radical reactions based on a simple valence-bond method, we have carried out only a limited number of preliminary calculations with a one-electron method for the primary step:[30]
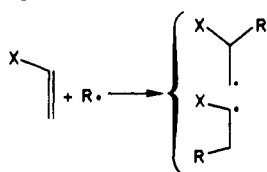
The two different products are obtained by approaching R perpendicular to the olefinic plane, either directly above one carbon atom or directly above the other. We used a restricted open-shell self-consistent field version of the GAUSSIAN 70 program,[31] similar to that of Binkley, Pople, and Dobosh.[32] All the orbitals but one are doubly occupied, while the odd orbital ψ_a, with energy ϵ_a has a single electron. The total energy of the corresponding doublet state is given by:

$$E = E_{SCF} - \frac{1}{4} J_{aa} \qquad (17)$$

where E_{SCF} is the expectation value of the Nesbet type Hartree-Fock operator

$$F = h + \sum_{j<a} (2J_j - K_j) + J_a - \frac{1}{2} K_a \qquad (18)$$

(the integral J_{aa} is the self-energy of an electron in ψ_a; h, J, and K are respectively the usual one-electron, Coulomb, and exchange operators).

Olefins substituted by X = BH_2, CN, F, CH_3, and NH_2 were considered. The corresponding double-bond polarizations, together with the net π charge transfer from carbon α to carbon β, are shown below:[33]
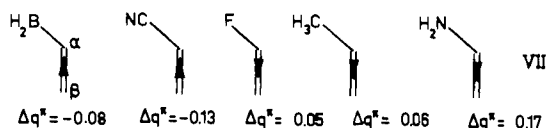
The π polarization and net charge transfer in a molecule like propylene is only partly due to the donor character of the substituent; it also arises from second-order mixing of π with π^* through the interaction of both with the methyl orbitals.[28]

For two of the systems shown above (X = BH_2, NH_2), there may not actually be addition on the double bond. However, they are included so as to provide us with a wide range of substituent electronegativities to illustrate the theory. The initial polarizations shown above are used as *indicators* to help us interpret the calculated preferred direction of attack within the framework of diagrams III, IV, V, and VI. Of course, as

Table I. Difference in Activation Energies $E^{\ddagger}_{subs} - E^{\ddagger}_{unsubs}$ (kcal/mol) Between Free-Radical Addition at Substituted Carbon and Addition at Unsubstituted Carbon in H(X)C=CH$_2$

X	Reagent	
	Cl·	H·
BH$_2$	−2 (contrathermod)	+1
CN	−1 (contrathermod)	+1
F	+5.4	+4
CH$_3$	+4	+3
NH$_2$	+12	+9

seen as the reagent approaches, the charge distribution changes and odd-electron density starts appearing on the double bond.[34]

We consider first the attack of a chlorine atom. During the approach of the radical, bond lengths of the substrate and bond angles are allowed to relax from their initial to their final values. For X = CH$_3$ or NH$_2$, attack is preferred on the unsubstituted end, giving the thermodynamically preferred product. The potential energy curves for chlorine plus propylene are shown in Figure 5a. The curves remain roughly parallel throughout the reaction path. But for X = BH$_2$ and CN, attack on the substituted position becomes competitive with that on the unsubstituted position and seems even to be very slightly favored. The potential energy curves for chlorine plus vinylborane are shown in Figure 5b. The contrathermodynamic nature of the lower transition state is now reflected by a crossing between the curves on the side of primary product. Although the C=C bond length and the ClCC angle are relaxed as the reagent approaches, the activation energy calculated for addition ($\approx$25 kcal/mol) is far too large. Chlorine atoms add faster than they abstract, so $E^{\ddagger}$ (addition) is probably less than 4 kcal/mol.[35] The minimal nature of the basis set is undoubtedly responsible for the major part of the error.

We consider next the attack of a hydrogen atom. In this case, for all five substituted olefins, preferred attack is on the unsubstituted end, giving the thermodynamically more stable product. The results for Cl· and H· are summarized in Table I.

Table I illustrates the role of the relative electronegativity of attacking reagent and substrate sites. This role has very recently been emphasized by Tedder and Walton,[36] who state that "The polar influences which we have found to be important can be expressed in terms of the electronegativity difference between the radical and the attacked site on the olefin". Here we find that for a highly electronegative reagent contrathermodynamic attack tends to occur for π-acceptor substituents, while for donor substituents, the reinforcement of thermodynamic control by polar effects appears clearly in the higher difference calculated for Cl· addition than for H· addition. For an "electroneutral" reagent thermodynamic control seems to predominate. The qualitative agreement between the ab initio one-electron minimal basis set calculations and the previously described valence-bond like model is surprising and encouraging.

A further, more quantitative comparison can be made with the experimental data.[36] We consider the addition of CF$_3$· and CH$_3$· to the fluoroethylenes FHC=CH$_2$ and FHC=CF$_2$. The model predicts that the highly electronegative CF$_3$· radical should add preferentially to the unsubstituted CH$_2$ end of vinyl fluoride and to the less substituted CHF end of trifluoroethylene (a fluorine atom behaves like a π *donor*, see VII). For the CH$_3$· radical, which is weakly electropositive, one can expect either weak thermodynamic control or even contrathermodynamic control. The former appears to occur in FCH=CH$_2$
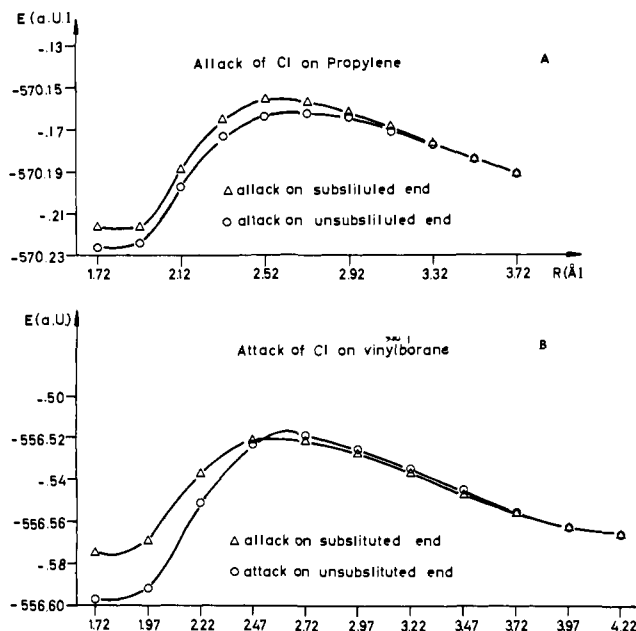
Figure 5.

Figure 6. Hückel state energies for symmetrical approach of bond 3-4 to bond 1-2.

Table II. Differences in Activation Energies and Orientation Ratios for the Addition of Radicals to Fluoroethylenes

| | $E^{\ddagger}{}_{subs} - E^{\ddagger}{}_{unsubs}$ | Orientation ratio | |
System	(kcal/mol)	Calcd[a]	Exptl[b]
$FHC=CH_2 + CF_3\cdot$	4.5	0.005	0.09
$FHC=CH_2 + CH_3\cdot$	3.1	0.025	0.20
$FHC=CF_2 + CF_3\cdot$	2.3	0.065	0.50
$FHC=CF_2 + CH_3\cdot$	~0	~1	2.10

[a] The calculated orientation ratio is assumed to be $\exp[-(E^{\ddagger}{}_{subs} - E^{\ddagger}{}_{unsubs})/kT]$ with $T = 423K$. (In trifluoroethylene the "substituted" end is the more substituted CF_2 end of the olefin.) [b] Reference 36, Table I.

(attack at CH_2),[36] the latter in $FHC=CF_2$ (attack at the more substituted and more π positive CF_2 end, giving the less stable radical).[36] Hence there is excellent agreement between the qualitative theory and the experimental results.

The ab initio minimal basis set calculations fall in line with the qualitative predictions, except for the attack of $CH_3\cdot$ on trifluoroethylene, where no preferential site of attack is found. In Table II we compare the ab initio "orientation ratios" with the experimental results given by Tedder and Walton.[36] Although, as mentioned previously, the absolute values of the activation energies are too large, the differences reproduce qualitatively the experimental trend.

Appendix

Valence Bond and Hückel Description of Four-Center Four-Electron System. In order to compare the specific features of odd-electron and even-elec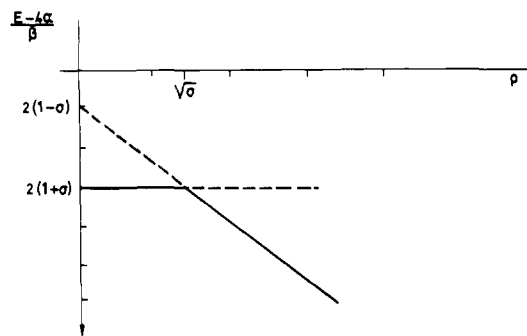tron systems, let us briefly review the valence-bond and Hückel schemes for the following four electron four-center array (compare ref 7c):

The energies of two singlet states in the valence bond model have the form:

$$E_{I,II} = A - \frac{1}{3} \sum_{i<j=1}^{4} Z_{ij}$$

$$\pm \frac{1}{\sqrt{2}} [(\alpha' - \beta')^2 + (\beta' - \gamma')^2 + (\gamma' - \alpha')^2]^{1/2} \quad (A1)$$

where

$$\alpha' = J_{12} + J_{34} - \frac{2}{3}(Z_{12} + Z_{34})$$

$$\beta' = J_{14} + J_{23} - \frac{2}{3}(Z_{14} + Z_{23}) \quad (A2)$$

$$\gamma' = J_{13} + J_{24} - \frac{2}{3}(Z_{13} + Z_{24})$$

The quantities A, J_{ij} and Z_{ij} are defined as:

$$\langle D_{ij}^{kl} | H | D_{ij}^{kl} \rangle = A - J_{ij} - J_{kl}$$

$$\langle D_{ij}^{kl} | H | D_{il}^{kj} \rangle = J_{lj} - Z_{lj} \quad (A3)$$

with the Slater determinant defined in a similar way as for the three-center three-electron system (down indexes label α spins, up indexes label β spins). Note the formal similarity of eq A1 and 6. The energy expression A1 has been obtained under assumption that the Slater determinants are orthogonal functions and that $\langle D_{ij}^{kl} | H | D_{kl}^{ij} \rangle \approx 0$. This assumption implies neglect of terms of higher order than first in overlap integrals. The quantities J_{lj} and Z_{lj} are of even and odd power in the overlap density, respectively.

The energy describing the symmetrical approach of two bonds can be simply written:

$$E = A - \frac{2}{3}(Z_{12} + Z_{13}) \mp 2\left(J_{12} - \frac{2}{3}Z_{12}\right)$$

$$\times (1 + x^2 - x)^{1/2} \quad (A4)$$

where $x = \alpha'/\gamma'$ and next-nearest-neighbor interactions are neglected; $\beta' \approx 0$. The barrier arising from the last term of eq A4 is roughly twice the barrier drawn in Figure 1 which illustrates the colinear approach of the radical center to the bond. In conventional valence-bond theory the energy of the lowest singlet for the square arrangement is equal to the energy of two bonds at infinite distance from each other. Here, in our model, $\Delta E = \Delta A - 2Z_{12}$, which shows a destabilization for

a Hückel array (but a stabilization for a Mobius array; compare ref 23).

The energies of the lowest states in the Hückel model for the symmetrical approach of bond 3-4 to bond 1-2 are $E = 4\alpha + 2\beta_{12}(1 + \sigma)$ and $E = 4\alpha + 2\beta_{12}[(1 + \sigma)^2 + 4\rho^2]^{1/2}$ with $\sigma = \beta_{34}/\beta_{12}$ and $\rho = \beta_{13}/\beta_{12} = \beta_{24}/\beta_{12}$. There is a crossing of the lowest singlets for $\rho = \sqrt{\sigma}$, without any energy barrier (Figure 6).

The situation for the four-electron four-center square array is similar to that of the three-electron three-center linear array: our valence-bond model gives rise to a small energy barrier (but no crossing between states) while the Hückel model gives no barrier but intersecting states. The state crossing for the square geometry in the Hückel approximation can be avoided by taking into account correlation effects, because the Slater determinants built from MO's belong to the reducible representation $E^2 = A_1 + A_2 + B_1 + B_2$ of the symmetry group C_{4v}.[37]

References and Notes

(1) (a) Institut für Physikalische Chemie; (b) Laboratoire de Chimie Théorique (ERA 549 associated with the CNRS).

(2) Well-known books include (a) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957; (b) W. A. Pryor, "Free Radicals", McGraw Hill, New York, N.Y., 1966; (c) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions", Wiley-Interscience, New York, N.Y., 1971; (d) "Free Radicals", Vol. I and II, J. Kochi, Ed., Wiley, New York, N.Y., 1973; (e) D. C. Nonhebel and J. C. Walton, "Free Radical Chemistry", Cambridge University Press, Cambridge, Mass., 1974.

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(33) We have already justified the choice of π, rather than total, polarization and charge transfer. For cyanoethylene, the overall polarization actually opposes the π polarization; yet the calculated pathways (see further) are consistent with the latter.

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