Origins of Nonperfect Synchronization in the Lowest-Energy Path of Identity Proton Transfer Reactions Leading to Delocalized Anions: A VBSCF Study[1]

Nathan Harris,[‡,§] Wu Wei,[‡,||] William H. Saunders, Jr.,*[,⊥] and Sason Shaik*[,‡]

Contribution from the Department of Organic Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University, Jerusalem, 91904 Israel, Department of Chemistry, The State Key Laboratory for Physical Chemistry of Solid Surfaces and Institute of Physical Chemistry, Xiamen University, Xiamen 361005, P. R. China, and Department of Chemistry, University of Rochester, Rochester, New York 14627

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Abstract: Two proton-transfer reactions yielding delocalized conjugate bases, the identity reactions of allyl anion with propene (**2a**) and acetaldehyde enolate with acetaldehyde (**2b**), are examined by means of quantum-chemical calculations and compared with another proton-transfer yielding a localized anion, methide ion with methane (**9**). When both reactants and transition structures are constrained to conformations that prevent delocalization, barriers are lower, showing that delocalization stabilizes the anions more than the transition structures. Calculations utilizing valence bond self-consistent field (VBSCF) methods show that in all three cases the single most important contributing structure to the hybrid is a triple ion species $R^- \ H^+ \ R^-$. This mixes well with localized covalent structures $R{-}H \ R^-$ and $R^- \ H{-}R$, but poorly with delocalized covalent or triple ion structures. It is concluded that nonperfect synchronization in **2a** and **2b** results from a balance between maximizing resonance stabilization and maximizing covalent carbon−hydrogen bonding in the $(R{\text{- - -}}H{\text{- - -}}R)^-$ transition structure.

We wish to report direct computational evidence that the lag in delocalization at the transition state in proton transfers from carbon acids yielding delocalized anions results from a balance between maximizing resonance stabilization and maximizing covalent bonding in the transition structure. It does not, contrary to a common assumption, deprive the transition structure of resonance stabilization that might otherwise lower the barrier.

The first systematic discussion of the lag in delocalization that occurs in deprotonation of carbon acids such as nitromethane was by Kresge.[2] The evidence he sought to explain was that the equilibrium acidity of nitroalkanes increases in the order nitromethane < nitroethane < 2-nitropropane, but the rate of proton abstraction decreases in the same order. This suggests that negative charge remains largely localized on the α-carbon atom in the transition structure but is relayed out to the oxygens in the product anions. He argued that the lag in delocalization of the negative charge arose because rehybridization in the transition structure was incomplete and thus only a fraction of the charge transferred from base to substrate could be delocalized within the developing conjugate base. This argument has been extended and quantified by Bernasconi as the Principle of Nonperfect Synchronization (PNS).[3] While the principle provides a rigorous way of describing the phenomenon, it has never been clear why the reaction should choose this energy path when the fully synchronous and presumably lower-energy path seemed in principle to be available. If more delocalization and hence more stabilization could be gained by more complete rehybridization in the transition state, why is rehybridization as limited as it is? Unease on this point is apparent in the statement "This state of affairs seems to contradict a basic law of nature, according to which physical or chemical processes should always follow a path of minimum energy".[4] Clearly neither Bernasconi nor anyone else seriously believes that the PNS violates a basic law of nature, but why it should even appear to has remained a worrisome question.

Qualitative paradigms that avoid this difficulty have been available for some time. Hine used the Principle of Least Nuclear Motion to argue that the geometric changes required in going from the reactant to the transition structure would increase the energy of a valence bond contributor with a reactant-like electron distribution and thus increase the barrier.[5] A crucial point was made by Pross and Shaik, who argued that an important contributor to the resonance hybrid transition structure in the deprotonation of nitromethane should be a triple ion species, **1**, which would both lower the energy of the transition structure and lead to localization of charge on the carbon of the developing nitromethanate anion.[6] By this analysis

$$B{:}^- \ H^+ \ {}^-{:}CH_2NO_2$$

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[‡] The Hebrew University.

[§] Present address 6509 Marsol Road, Apartment #620 Mayfield Heights, OH 44124.

[||] Xiamen University.

[⊥] University of Rochester, Rochester.

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a hypothetical synchronous transition structure would have a *higher* barrier than the actual one, and the dilemma inherent in the PNS would vanish.

Recent computational evidence has made it clear that the lag in delocalization is an intrinsic property of the reactions that persists in the gas phase.[3,7] The present study utilizes two approaches. One is to analyze further two of the systems previously studied by ab initio Gaussian[8] calculations by comparing localized and delocalized reactants and transition structures. The other and more important approach is to apply valence bond (VB) calculations to determine the relative importance of the various VB contributors to the optimized structure and how they affect the energy of that structure. Finally we compare the VB calculations on proton transfers giving delocalized anions with those on a proton-transfer giving a localized conjugate base, methide anion + methane.

Computational Methods

Preliminary structures were obtained using Gaussian 94[8] and Gaussian 98.[9] The standard 6-31+G basis set was used.[10] Dihedral angles of the optimized structures were modified slightly so as to facilitate separation of the π orbitals from the σ framework. The energetic effects of these changes were negligible (<1 kcal mol^{-1}). We next transformed the integrals from the Gaussian calculations to a valence bond basis set utilizing the Xiamen programs.[11] In this process the active atomic orbitals are those involved in the proton transfer (s and p_y orbitals on the carbons and oxygens and s orbitals on the transferred proton). Molecular orbitals with large coefficients for these atomic orbitals were chosen as the active space (four molecular orbitals for the propene−allyl anion and acetaldehyde−acetaldehyde enolate transition structures, and two for the methane−methide transition structure). The remaining molecular orbitals and the inner-shell 1s orbitals on the carbons and oxygens were frozen. Contributing valence bond structures were constructed from the active atomic orbitals, and the resulting orbitals and structure coefficients were simultaneously optimized using the VBSCF procedure in the Xiamen programs.

Table 1. Proton Transfers without and with Delocalization

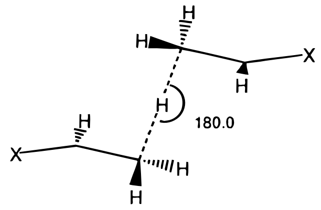
quantity[a]	CH_4	$CH_3CH{=}CH_2$	$CH_3CH{=}O$
ΔE_A(loc)	426.5	422.1	409.2
ΔE_A(deloc)		398.7	372.3
ΔE_{TS}(loc)	13.1	6.6	−0.7
ΔE_{TS}(deloc)		8.5	2.5

[a] Energies in kcal mol^{-1} from calculations at MP2/6-31+G*//MP2/6-31+G*. ΔE_A is acidity at 0 K, ΔE_{TS} is the energy difference between TS and separated reactants at 0 K.

Results and Discussion

Our earlier Gaussian calculations[7] show that barriers to deprotonation of acids that yield delocalized anions are higher than barriers to deprotonation of acids of comparable acidity that yield localized anions. A more direct comparison can be made if delocalization can be shut down. This is possible with allyl anion and acetaldehyde enolate by enforcing conformations in which the unshared pair on carbon is orthogonal to the π system. This was done for both the anions and the transition structures while allowing all other parameters to optimize. The results are shown in Table 1. Energies are reported rather than enthalpies because the species involved are not stationary states.

As expected, the localized species show much lower acidities (ΔE_A) than the delocalized ones. The vinyl and carbonyl groups do exert inductive effects that enhance acidity modestly relative to methane, but delocalization provides a much larger acidity-enhancing effect. The barriers to deprotonation (ΔE_{TS}), however, are lower by ~2 kcal for the localized cases because delocalization stabilizes the conjugate bases more than the transition structures. Thus, a direct comparison of structures that differ only conformationally demonstrates that the transition structures gain less energy from delocalization than do the stable anions. The molecular orbital calculations afford no indication of why this is the case. While they are capable of showing with considerable accuracy what the minimum energy species is, they tell us little of why and how it reached that state.



2 (a, X = CH$_2$; b, X = O)

To achieve more insight into this process we turn to VB calculations. The transition structures are **2a** and **2b**. Appropriate fragments were built up from the active atomic orbitals and in turn used to construct the VB contributors to the transition state structures. The fragments required are **3−8**

$X{=}CH{-}CH_2{-}H$ **3** $H{-}CH_2{-}CH{=}X$ **4** $^{-}{:}CH_2{-}CH{=}X$ **5** $X{=}CH{-}CH_2{:}^{-}$ **6**

$CH_2{=}CH{-}X{:}^{-}$ **7** $^{-}{:}X{-}CH{=}CH_2$ **8**

(the fragment H$^+$ bears no electrons and thus does not need to be included in the set). The localized VB method (LVB) keeps the basis functions strictly localized in the contributing struc-

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Scheme 1. Weights of Contributing Structures from VBSCF Calculations on the Propene to Allyl Anion and Acetaldehyde to Acetaldehyde Enolate Identity Reaction Proton Transfers[a]

$\mathrm{X{=}CH\text{-}CH_2\text{-}H\ \ ^{-}{:}CH_2\text{-}CH{=}X}$ $\quad$ $\mathrm{X{=}CH\text{-}CH_2{:}^{-}\ \ H\text{-}CH_2\text{-}CH{=}X}$

ϕ_1 (0.187, 0.208) $\quad$ ϕ_3 (0.187, 0.208)

[0.151, 0.248] $\quad$ [0.151, 0.248]

$\mathrm{X{=}CH\text{-}CH_2\text{-}H\ \ CH_2{=}CH\text{-}X{:}^{-}}$ $\quad$ $\mathrm{^{-}{:}X\text{-}CH{=}CH_2\ \ H\text{-}CH_2\text{-}CH{=}X}$

ϕ_2 (0.049, 0.016) $\quad$ ϕ_4 (0.049, 0.016)

[0.118, 0.008] $\quad$ [0.118, 0.008]

$\mathrm{X{=}CH\text{-}CH_2{:}^{-}\ \ H^{+}\ \ ^{-}{:}CH_2\text{-}CH{=}X}$

ϕ_5 (0.402, 0.540)

[0.229, 0.543]

$\mathrm{X{=}CH\text{-}CH_2{:}^{-}\ H^{+}\ CH_2{=}CH\text{-}X{:}^{-}}$ $\quad$ $\mathrm{^{-}{:}X\text{-}CH{=}CH_2\ \ H^{+}\ ^{-}{:}CH_2\text{-}CH{=}X}$

ϕ_6 (0.059, 0.006) $\quad$ ϕ_7 (0.059, 0.006)

[0.102, -0.028] $\quad$ [0.102, -0.028]

$\mathrm{^{-}{:}X\text{-}CH{=}CH_2\ \ H^{+}\ \ CH_2{=}CH\text{-}X{:}^{-}}$

ϕ_8 (0.006, -0.001)

[0.029, -0.0003]

[a] Weights in parentheses refer to the allyl anion + propene reaction ($X = CH_2$); weights in brackets refer to the acetaldehyde enolate + acetaldehyde reaction ($X = O$). The first weight in each list refers to calculations by the localized valence bond method (LVB); the second refers to the delocalized valence bond (DVB) or Coulson-Fischer method (see text).

tures. However, LVB requires many VB structures to give quantitative accuracy. A refinement that significantly lowers the VB energies of the hybrids is to allow slight delocalization of the basis functions (p_y functions in the present case) on a given carbon or oxygen atom to adjacent carbon or oxygen atoms.[12] This allows the bonding electrons to delocalize, and provides a better description of polar bonds. We will henceforth refer to this as the delocalized VB (DVB) method. Resonance hybrids consisting of two to eight or more contributing structures were constructed from the set of VB contributors. It was found that at least five contributing structures are needed to give a proper description of the transition structure, although three additional structures provide a further decrease in energy at the LVB level. Weights of the contributing structures for the eight-structure case are shown in Scheme 1. The numbers in parentheses refer to **2a**, while the numbers in brackets refer to **2b**. The first number in each list of two is the weight for the LVB method. We will discuss these numbers first.

An immediately obvious point is that the triple ion structure ϕ_5 is by far the most important single contributor to the hybrid and that it outweighs the symmetrically equivalent structures ϕ_1 and ϕ_3. Another is that localized structures (ϕ_1, ϕ_3, and ϕ_5) outweigh the ones that by mixing will cause delocalization of the $XCHCH_2$ moieties (ϕ_2, ϕ_4, ϕ_6, ϕ_7, and ϕ_8). Thus, the transition structure is dominated by localized contributors. A quantitative measure of this dominance can be obtained by summing up the weights of structures containing localized anionic fragments. Because ϕ_6 and ϕ_7 contain both localized and delocalized fragments, half of their weights are assigned to the localized category. By this criterion, **2a** is 84% localized, and **2b** is 63% localized. This order is intuitively reasonable because a negative charge should be more easily accommodated on the terminal oxygens of **2b** than on the terminal carbons of **2a**. Both transition structures are well short of the degree of delocalization in the corresponding conjugate bases; allyl anion is 50% and acetaldehyde enolate 31% localized.

We showed earlier that enforcing complete delocalization in the allylic fragments of the transition structure **2a** raised the energy by 8.2 kcal mol^{-1}.[1] While this is a somewhat artificial model, because the two ends of the allylic fragments in the transition structure are not identical as they are in allyl anion, neverthless the approximation may not be too bad. An estimate of the effect of this unsymmetry was obtained for **2b** by constructing a hybrid of ϕ_1 and ϕ_2, which should be a good model for an acetaldehyde enolate anion with its carbon atom next to the α-hydrogen of an acetaldehyde molecule. The enolate portion is 26% localized compared to 31% for an isolated enolate ion and 63% for the $\phi_1-\phi_8$ hybrid of the transition structure. The unsymmetry effect thus works against rather than for localization, and further validates the conclusion that a hypothetical species less localized than the optimum transition structure must be of higher energy.

If we turn now to the results from the DVB method (the second number in each list of two in Scheme 1), we see that the contributions from localized structures increase and those from delocalized structures decrease relative to the LVB results. In fact, **2b** appears to show no delocalization at all, while **2a** is close behind with only 4% delocalization. The DVB method reduces substantially the need to consider formally delocalized structures and is consequently less suitable than the LVB method for assessing the importance of delocalized contributors. The relative proportions of covalent and triple ion structures vary much less with the method, remaining within 5% of 50:50 in both methods.

Fragments such as $^{-}{:}X{-}CH^{+}{-}CH_2{:}^{-}$ and $^{-}{:}X{-}CH^{+}{-}CH_2{-}H$ can be used to generate additional contributors. Up to 21 were tried with **2b** at the LVB level, but allowing for slight delocalization by the DVB method also allows implicitly for such polarization and gives a lower energy than that from larger numbers of contributors made up of strictly localized fragments.

In principle VBSCF calculations should give lower energies than molecular orbital calculations at HF levels, provided the basis sets are the same, because they allow for electron correlation by enforcing localization within a given VB contributor. Present computational limitations require freezing of all except a minimal number of active electrons in any but very small systems. The programs we use[11] are limited to 12 active electrons. In **2a** and **2b** we utilize eight active electrons, which means that most of the electrons and the corresponding orbitals must be frozen. Thus, the "inactive" electrons remain at the HF level and cannot adapt themselves to the changes of the wave function. Consequently, LVB calculations will in most cases give energies that are above the corresponding HF energies. The more flexible DVB calculations do better, but they still suffer from the need to freeze quite a few of the orbitals at their HF situations with currently available programs.

Table 2 lists the energies of selected hybrids and contributors relative to the corresponding HF/6-31+G energies. Negative values mean that the VB energy is lower, and vice versa for positive values. The first three entries refer to **2a** and the remainder to **2b**. For **2a** the LVB method gives an energy well above HF even with eight contributors, and the energies are

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Table 2. Energies in kcal mol^{-1} of Resonance Contributors to Transition Structures **2a** and **2b** Relative to HF/6-31+G

entry	structures	*E*(LVB)	*E*(DVB)
1	**2a**, ϕ_1–ϕ_8	57.3	−19.4
2	**2a**, ϕ_1–ϕ_5	70.6	−19.3
3	**2a**, ϕ_1, ϕ_3, ϕ_5	83.8	
4	**2b**, ϕ_1–ϕ_{21}	21.3	
5	**2b**, ϕ_1–ϕ_8	112.0	1.0
6	**2b**, ϕ_1–ϕ_5	137.6	3.0
7	**2b**, ϕ_1–ϕ_4	158.0	39.7
8	**2b**, ϕ_1, ϕ_3, ϕ_5	171.9	3.2
9	**2b**, ϕ_1, ϕ_3	208.0	45.7
10	**2b**, ϕ_1, ϕ_2	211.1	121.5
11	**2b**, ϕ_2, ϕ_4	234.4	67.6
12	**2b**, ϕ_2	241.0	126.2
13	**2b**, ϕ_5	253.0	75.0
14	**2b**, ϕ_1	295.0	122.4

still higher for five and three contributors. In contrast, the DVB method gives energies decisively below HF. Note that there is little difference between the hybrids with eight and five contributors, which shows further that the DVB method implicitly allows for a considerable degree of delocalization and converges at five structures.

The more extensive results on **2b** show a very similar pattern. With 21 contributors (entry 4), including species with polarized carbonyl groups and double bonds (vide supra), the LVB method gives an energy distinctly above HF. Even the DVB method (entry 5) gives only an energy close to HF, not below it, in contrast to **2a**. The DVB method shows little difference in energy between hybrids with three, five, and eight contributors, again demonstrating its ability to make implicit allowance for delocalization, and its virtual convergence already at five structures. For both the LVB and DVB methods, inclusion of the triple ion structure ϕ_5 (entry 8) leads to a substantial lowering of energy, in line with the heavy weight of this structure in Scheme 1. The energy value for ϕ_1 (entry 14) represents the point along the reaction coordinate at which curves representing the energies of reactants (ϕ_1) and products (ϕ_3) cross. The hybrid of ϕ_1 and ϕ_3 thus already gains substantial resonance energy, and inclusion of ϕ_5 affords a sizable further lowering (compare entries 9 and 8).

For comparison with these delocalizable systems, we chose the simplest localized carbon-to-carbon proton transfer, methane + methide anion, **9**.

$$(H_3C\text{- - -}H\text{- - -}CH_3)^-$$

9

The problem can be simplified by constructing H_3 hybrids of the non-transferred hydrogens at either end, thus limiting the system to the C−H−C (p_z) axis so that only s and p_z orbitals need be considered. Calculations were done at the LVB level for the three contributors **10**, **11**, and **12**.

$H_3C{-}H\ ^{-}{:}CH_3$ **10** $H_3C{:}^{-}\ H{-}CH_3$ **11** $H_3C{:}^{-}\ H^{+}\ ^{-}{:}CH_3$ **12**

Higher-energy contributors were tried but afford only slight further gains in energy. Calculations were also done at a more sophisticated level called the breathing orbital method (BOVB)[13] in which a CH_3 covalently bonded to a hydrogen is allowed to optimize separately from a CH_3 in a methide ion. In a hybrid of **10** and **11** the weights are equivalent at 0.500. In a hybrid of all three, the triple ion structure **12** is of major importance, with a weight of 0.574 by LVB and 0.512 by BOVB. It is of a weight equal to or greater than those of **10** and **11,** taken together. The importance of a triple ion contributor thus seems general for carbon-to-carbon proton transfers, not just those leading to delocalized anions.

Table 3. Energies in kcal mol^{-1} of Resonance Contributors to Transition Structure **9** Relative to HF/6-31+G

structures	*E*(LVB)	*E*(BOVB)
10, **11**, **12**	0.4	−3.5
10, **11**	35.2	22.3
12	64.4	64.4
10 or **11**	121.1	92.3

The energies of the contributors and hybrids are listed in Table 3. The triple ion structure **12** is lower in energy than either of the covalent structures **10** and **11**, and including it in the hybrid lowers the energy substantially. The BOVB method lowers the energies of the hybrids relative to the LVB method, although it does not have the dramatic effect that the DVB method has with **2a** and **2b**.

We return now to the important question of why delocalization is limited in **2a** and **2b**. This point can best be discussed with reference to Figure 1. Figure 1 illustrates the situation for **2b**, but a similar Figure applies for **2a** and was used in ref 1. The two figures and the conclusions from them are qualitatively similar, and thus only **2b** will be discussed here. The energies in the following discussion are all from LVB calculations unless otherwise noted.

As a rule, for two structures to mix strongly and give a low-energy hybrid they should be close in energy but should also overlap well. Two symmetry-equivalent structures are of identical energy and should mix optimally, provided they overlap well. Otherwise, non-equivalent structures mix according to the rules of perturbation theory, proportional to the overlap and inversely proportional to the energy gap of the structures.

Figure 1a shows the mixing patterns of the covalent contributors to the resonance hybrid. The overlap between the two structures is less for ϕ_2 and ϕ_4 than for ϕ_1 and ϕ_3, and this gives $\phi_{1,3}$ a more than 80 kcal advantage over $\phi_{2,4}$ in mixing energy. The extent of overlap is roughly inversely related to the distance over which an electron must be transferred to interconvert the two structures, and that distance is greater for ϕ_2 and ϕ_4 than for ϕ_1 and ϕ_3.[14] Note in Table 2 that ϕ_2 is actually lower in energy than ϕ_1, presumably because oxygen can more easily bear a negative charge than carbon. Poor mixing, however, makes $\phi_{2,4}$ *higher* in energy than $\phi_{1,3}$.

Of the remaining structures (ϕ_5–ϕ_8) the most important single contributor is the triple-ion species ϕ_5. When this is mixed with $\phi_{1,3}$ (Figure 1b), the energy of mixing is 36.0 kcal and the resulting structure, ψ_{local}, is still completely localized. This can in turn be mixed with delocalized structures $\phi_{2,4}$, $\phi_{6,7}$, and ϕ_8. While this mixing affords a further 60.0 kcal of stabilization, the delocalized structures are all of substantially higher energy than ψ_{local} and contribute considerably less to the structure of the hybrid. The delocalized triple ion species $\phi_{6,7}$, and ϕ_8 are of particularly high energy because the separation of positive and negative charges is much greater than in ϕ_5.

There is a price to be paid for the predominance of the triple ion structure, ϕ_5, for it lacks the C−H bond energy of the covalent species ϕ_1–ϕ_4. The price, however, is less than would be incurred by omitting it. A hybrid consisting only of structures that preserve the C−H bonding, ϕ_1–ϕ_4, is 20.4 kcal above

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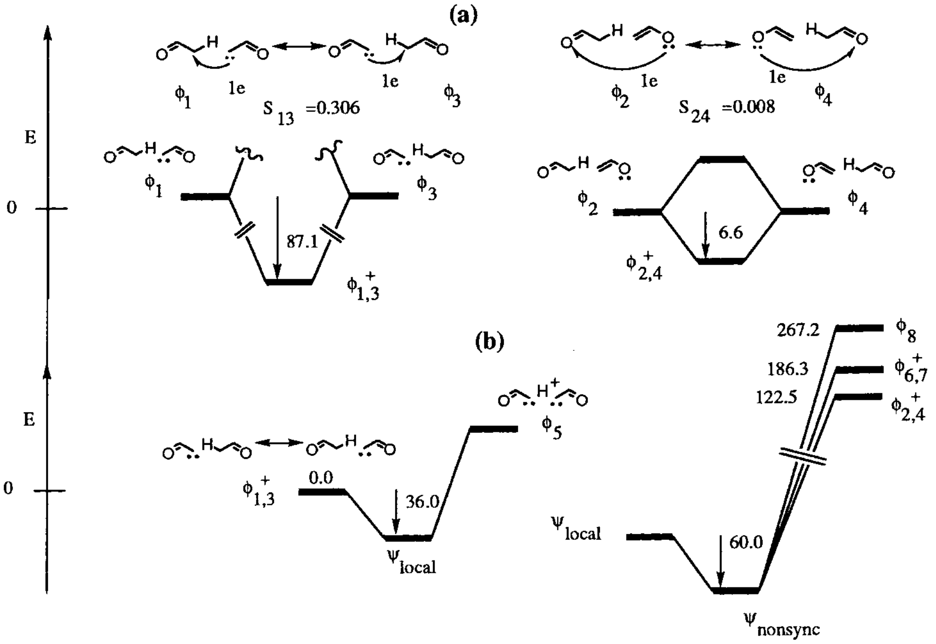

Figure 1. VB interaction diagrams with relative energies in kcal mol^{-1}. (a) Mixing of the degenerate structures ϕ_1 and ϕ_3 gives the hybrid $\phi_{1,3}$. Similar mixing of ϕ_2 and ϕ_4 gives the hybrid $\phi_{2,4}$. Strength of mixing is related to the overlaps S_{13} and S_{24}. (b) Mixing of hybrid $\phi_{1,3}$ with triple ion ϕ_5 gives localized structure ψ_{local}. Weak mixing of ψ_{local} with high energy structures $\phi_{2,4}$, $\phi_{6,7}$, and ϕ_8 gives the nonsynchronous structure ψ_{nonsync}.

$\phi_1-\phi_5$ and is still 60% localized because of the poor $\phi_2-\phi_4$ mixing (vide supra). The VB mixing then must determine the optimum balance between maximizing the strength of the C$-$H$-$C bonding, which would limit the contributing structures to $\phi_{1,3}$ and $\phi_{2,4}$, and allowing maximum resonance stabilization by inclusion of triple ion structures (particularly ϕ_5) in the hybrid that constitutes the transition structure. Inclusion of the triple ion structures reinforces the tendency toward localization that is already apparent in $\phi_1-\phi_4$, and results in the degree of nonperfect synchronization observed for $\phi_1-\phi_8$.

To summarize, the stabilities of the contributing structures and the mixing between them can be described in terms of qualitative valence bond arguments deduced from VBSCF calculations. In this way one can arrive at a satisfying rationalization of nonperfect synchronization. When one can see that the system utilizes as much resonance stabilization as possible without incurring energetic penalties, nonperfect synchronization no longer seems counterintuitive.

The lower C$-$H$-$C bond strength in the transition structure than in the substrate is very likely a major reason that carbon acids show higher barriers to deprotonation than Eigen acids. Support for this assertion is afforded by a comparison of **9** with the isoelectronic transition structure **13** for proton transfer from ammonium ion to ammonia.

$$(H_3N\text{- - -}H\text{- - -}NH_3)^+$$

13

The weight of the triple ion structure increases from 0.410 to 0.512 on going from the ion$-$dipole complex $(CH_4\text{- - -}CH_3)^-$ to **9**. The corresponding increase from $(NH_4\text{- - -}NH_3)^+$ to the transition structure **13** is 0.582 to 0.615.[15] Even though the N- - -H bond is more ionic than the C- - -H bond in the transition structure, the change from the reactant complex is less so that less covalent bonding is lost, and the barrier to reaction is lower than in the reaction at carbon.

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Supporting Information Available: *Z*-matrices and energies of species optimized by Gaussian calculations. Partial output files for VBSCF calculations on all important species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Unpublished results in these research groups.