JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 259–262 (1999)

Short Communication

Origins of non-perfect synchronization in the lowest energy path of the identity proton transfer reaction of allyl anion + propene: a VBSCF study

Nathan Harris,[1] Wu Wei,[1,2] William H. Saunders, Jr[3]* and Sason Shaik[1]

[1]Department of Organic Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University, Jerusalem 91904, Israel
[2]Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, China
[3]Department of Chemistry, University of Rochester, Rochester, New York 14627, USA

Received 22 October 1998; revised 13 November 1998; accepted 7 December 1998

ABSTRACT: Direct computational evidence is presented that the lag in delocalization at the transition state in proton transfers from carbon acids yielding delocalized anions provides the lowest energy path. It does not, contrary to a common assumption, deprive the transition structure of all resonance stabilization that could otherwise lower the barrier. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: non-perfect synchronization; identity proton transfer; resonance stabilization, VBSCF; delocalization

Kresge[1] suggested that the lag in delocalization in the deprotonation of carbon acids such as nitromethane arose because 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 and co-workers[2] as the principle of non-perfect synchronization (PNS). While the PNS provides a plausible analysis of the phenomenon, it has never been clear why a transition structure that makes greater use of the supposedly energy-lowering effect of delocalization is avoided.

Paradigms that provide qualitative reasons have been proposed. Hine[3] used the principle of least nuclear motion to argue that high barriers result from the geometric changes on going from the reactant to the transition structure which increase the energy of a valence bond (VB) contributor with a reactant-like electron distribution. This effect could be minimized by reducing delocalization and thereby geometric change. Pross and Shaik[4] pointed out 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 favor localization of charge on the carbon of the developing anion. Both suggestions have been largely ignored in the subsequent literature.

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

1

Recent computational evidence has demonstrated that the lag in delocalization is an intrinsic property that persists in the gas phase.[5,6] One of the systems studied by molecular orbital-based calculations, the identity reaction proton transfer from the methyl group of propene to allyl anion,[6b] shows the key characteristics of a reaction following the PNS. This reaction was chosen for further analysis by the VB method, with the aim of elucidating quantitatively why proton transfer and charge delocalization are non-synchronous, and to provide a general model of the phenomenon in terms of mixing of resonance structures into the wavefunction of the transition state.

The valence bond program from the Xiamen group is based on spin free valence bond theory, and its technical details can be found in the original literature.[7] Here we use the VBSCF procedure in which the orbitals and structure coefficients are optimized simultaneously to provide the lowest energy wavefunction for a given set of VB structures. The 6–31+G basis set was used.

The *trans-anti* transition structure **2** was altered slightly to make the C—C···H···C—C dihedral angle exactly 180° (we did not study the less symmetrical *gauche* transition structure[6]). This modification facilitates the separation of the π orbitals from the σ framework, and its energetic effect is negligible [<1 kcal mol^{-1} (1 kcal = 4.184 kJ)]. Six inner-shell s orbitals on

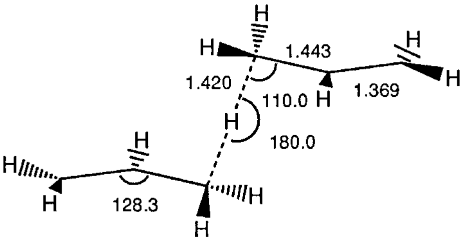
---

*Correspondence to: W. H. Saunders, Jr, Department of Chemistry, University of Rochester, Rochester, New York 14627, USA.

Contract/grant sponsor: ISF.
Contract/grant sponsor: VW Stiftung.

CCC 0894–3230/99/030259–04 $17.50

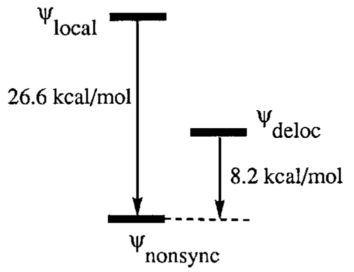
carbon plus ten C—H and four C—C σ orbitals were treated as a frozen core. The remaining four C—C π orbitals, including those that form the two carbanion-like centers and the orbitals associated with the migrating proton, were utilized in the VBSCF procedure.



2

After several attempts, we ascertained that the VBSCF energy converges with respect to the basis set of VB structures, and is lower than the corresponding HF energy The weights in Scheme 1 and the energies presented below are based on calculations in which the eight VB orbitals are constrained to be localized atomic functions on the six carbons and the migrating proton. VBSCF calculations of ϕ_1–ϕ_5 or ϕ_1–ϕ_8 allowing the VB orbitals to optimize freely give orbitals which are slightly delocalized and give a lower energy than HF. Such orbital optimization results in delocalization tails of the atomic functions and optimization is equivalent to inclusion of more VB structures in the set.[8] Energies in the two calculations are the same to within 0.1 mhartree (0.06 kcal mol^{-1}), and the weights of the structures using these unconstrained basis functions are in complete agreement with the weights in Scheme 1.

We now present the key features of the calculations. Scheme 1 shows the eight resonance structures that contribute to the description of the transition structure along with their weights in parentheses. (The coefficients for the seven non-orthogonal structures ϕ_1–ϕ_7 are −0.29, −0.14, −0.29, −0.14, 0.47, 0.16 and 0.16.)



Scheme 2

The members of the three ‘left–right’ resonance pairs in Scheme 1, (ϕ_1, ϕ_3), (ϕ_2, ϕ_4), (ϕ_6, ϕ_7), are related by symmetry and possess identical energies (i.e. $E_1 = E_3$, $E_2 = E_4$, $E_6 = E_7$). Mixing these pairs leads to the hybrid structures $\phi_{1,3}$, $\phi_{2,4}$, $\phi_{6,7}$.

It is striking that for each configuration type the weights are in favor of localization of the negative charge on the two allylic α-carbons and against delocalization of charge to the two γ-carbons. Thus the contributions of ($\phi_{1,3}$) are far more important than those of ($\phi_{2,4}$) and that of ϕ_5 is much larger than those of ($\phi_{6,7}$).

Clearly, our analysis of weights of contributing structures shows that the charge is not yet half delocalized, although the proton is half transferred. Thus, a variational VB calculation shows that these two different indicators of reaction progress do not vary synchronously.

Let us consider now the energetic cost of attaining a transition structure for which the proton transfer and charge delocalization are fully concerted. VB theory enables us to calculate such a putative transition structure by taking appropriately constrained linear combinations where the coefficients of the VB structures in Scheme 1 maintain the relations $c_1 = c_2$, $c_3 = c_4$ and $c_6 = c_7 = 1/2c_5$. As shown in Scheme 2, the energy of the fully

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

ϕ_1 (0.187) $\quad$ ϕ_3 (0.187)

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

ϕ_2 (0.049) $\quad$ ϕ_4 (0.0497)

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

ϕ_5 (0.402)

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

ϕ_6 (0.059) $\quad$ ϕ_7 (0.059)

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

ϕ_8 (0.006)

Scheme 1

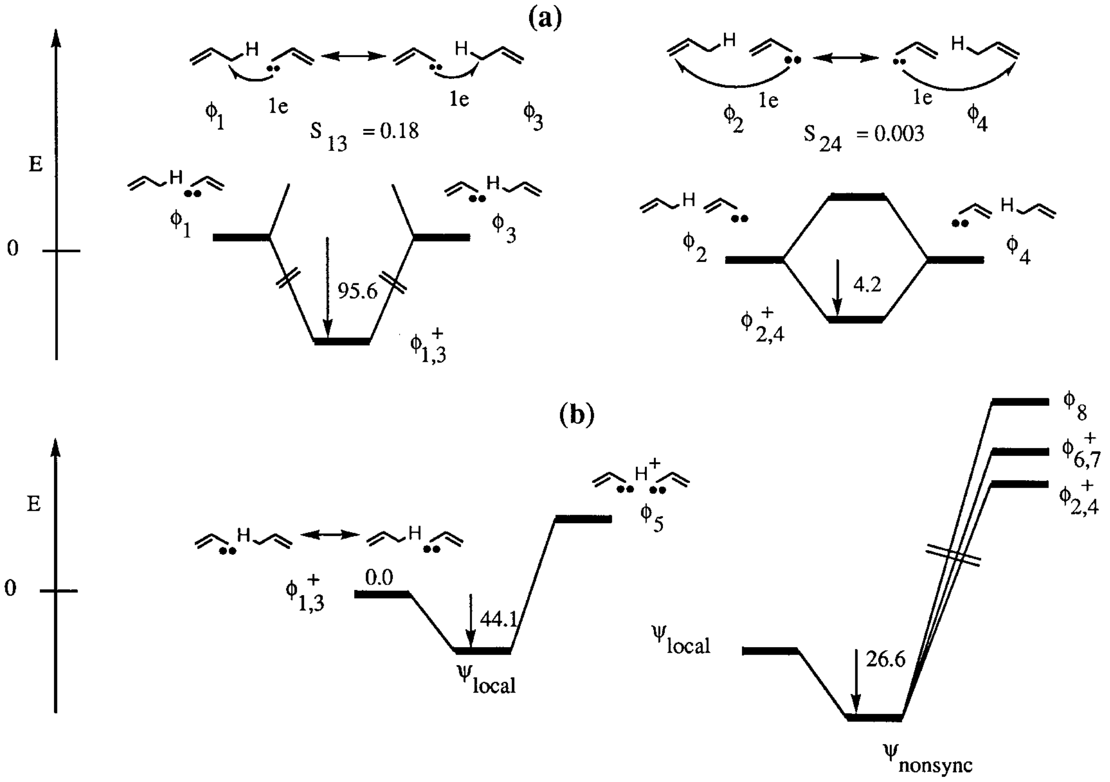


Figure 1. VB interaction diagrams with relative energies in kcal mol.$^{-1}$ (a) Mixing of the degenerate structures ϕ_1 and ϕ_3 gives resonating structure $\phi_{1,3}{}^{+}$. Similar mixing of ϕ_2 and ϕ_4 gives hybrid $\phi_{2,4}{}^{+}$. Strength of mixing is related to the overlaps S_{13} and S_{24}. (b) Mixing of stabilized 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 non-synchronous structure ψ_{nonsync}

delocalized hypothetical wavefunction is 8.2 kcal mol^{-1} higher than the optimum (non-synchronous) wavefunction. This gives a measure of the energy preference in favor of non-synchronicity. Another putative transition structure is the one with a fully localized wavefunction given by a linear combination of ϕ_1–ϕ_3, $\psi_{\text{local}} = (a\phi_5 + b\phi_{1,3}{}^{+})$. As seen in Scheme 2, the fully localized structure is 26.6 kcal mol^{-1} higher than the optimum structure formed from the full VB structure set ϕ_1–ϕ_8. It is apparent that a fully delocalized wavefunction has an energy in between those of a fully localized wavefunction and the non-synchronous wavefunction. It follows once more that non-synchronicity is a feature that optimizes the energy of the transition structure.

While non-synchronicity is clearly demonstrated in the foregoing discussion, it is still interesting to elucidate the underlying rules which determine the non-synchronicity. Let us analyze the mixing pattern of the different structures (ϕ_1–ϕ_8) in the VB wavefunction by appeal to Fig. 1.

In Fig. 1(a), the resonating pair of structures ϕ_1–ϕ_3 mixes to form hybrid symmetrized structures $\phi_{1,3}{}^{+}$ [and $\phi_{1,3}{}^{-}$, not shown in Fig. 1(a)]. The mixing is strong, in line with the large overlap between the two structures ($S_{13} = 0.18$), and results in a large stabilization of 95.6 kcal mol^{-1} [Fig. 1(a)]. On the other hand, the mixing between ϕ_2 and ϕ_4 is weak because of poor overlap ($S_{24} = 0.003$), and gives only a small stabilization of 4.2 kcal mol^{-1} for the hybrid. A similar weak mixing characterizes ϕ_6–ϕ_7 ($S_{67} = 0.03$). Hence the resonating hybrids $\phi_{2,4}{}^{+}$ and $\phi_{6,7}{}^{+}$ are barely stabilized because of poor overlap of the constituent structures, whereas $\phi_{1,3}{}^{+}$ is greatly stabilized for the opposite reason. Qualitatively, these overlaps are inversely proportional to the distance over which the electron is shifted to interconvert the constituent structures of each symmetrized hybrid.[9] Thus, a large overlap S_{13} is related to the small distance between the allylic α-carbons, while the small overlap S_{24} is related to the large distance between the allylic γ-carbons, etc.

Let us turn to the mixing patterns of the symmetrized hybrids with the triple ion structure, ϕ_5, in Fig. 1(b). The strongest interaction shown in Fig. 1(b) is between $\phi_{1,3}{}^{+}$ and ϕ_5. Two factors contribute to this. The first is their matrix element, which is large since their interconversion involves shifting electrons across the short C$_1$—H distances of the transition structure. The second factor is the $\phi_{1,3}{}^{+}$–ϕ_5 energy gap, which is small owing to the self-stabilization of $\phi_{1,3}{}^{+}$ [Fig. 1(a)]. Thus, the ϕ_5–$\phi_{1,3}{}^{+}$ interaction leads to an energy lowering of 44.1 kcal mol^{-1} and is the main interaction which sustains the delocalized C—H—C bonding of the transition state.

The resulting wavefunction, ψ_{local}, still has purely localized allylic moieties. It can achieve partial allylic delocalization by mixing with $\phi_{2,4}{}^{+}$, $\phi_{6,7}{}^{+}$ and ϕ_8, but these structures are high lying and possess poor matrix elements with ψ_{local}. Consequently, their mixings are rather weak, giving a total stabilization of 26.6 kcal mol^{-1} [Fig. 1(b)] in increments of 13.2, 12.6 and 0.8 kcal mol^{-1}.

It follows, therefore, that non-perfect synchronicity is an outcome of a selective mixing of the VB structures which constitute the electronic structure of the transition state. This selective VB mixing determines the optimum balance between maximizing the strength of the C_1—H—C_2 bond in the transition structure, and the conservation of delocalization in the allylic moieties. The result of this optimization is the non-synchronous wavefunction, ψ_{nonsync} [Fig. 1(b)], which follows the rules of variational VB mixing and has the optimum electronic structure for the transition state.

Acknowledgements

The research at the Hebrew University is supported in part by a grant from the ISF, established by the Israel Academy of Sciences, and in part by the VW Stiftung. The research at the University of Rochester is supported by NSF Grant CHE-9706242. W.H.S. thanks Professor Addy Pross for stimulating suggestions.

REFERENCES

1. (a) A. J. Kresge, *Chem. Soc. Rev.* **2**, 475–503 (1973); (b) A. J. Kresge, *Can. J. Chem.* **52**, 1897–1903 (1974).
2. (a) C. F. Bernasconi, *Acc. Chem. Res.* **20**, 301–308 (1987); (b) C. F. Bernasconi, *Acc. Chem. Res.* **25**, 9–16 (1992); (c) C. F. Bernasconi, *Adv. Phys. Org. Chem.* **27**, 119–238 (1992); (d) W. J. Albery, C. F. Bernasconi and A. J. Kresge, *J. Phys. Org. Chem.* **1**, 29–31 (1988).
3. J. Hine, *Adv. Phys. Org. Chem.* **15**, 1–61 (1977).
4. A. Pross and S. Shaik, *J. Am. Chem. Soc.* **104**, 1129–1130 (1982).
5. (a) C. F. Bernasconi and P. J. Wenzel, *J. Am. Chem. Soc.* **116**, 5405–5413 (1994); (b) C. F. Bernasconi and P. J. Wenzel, *J. Am. Chem. Soc.* **118**, 10494–10504 (1996); (c) C. F. Bernasconi, P. J. Wenzel, J. R. Keeffe and S. Gronert, *J. Am. Chem. Soc.* **119**, 4008–4020 (1997).
6. (a) W. H. Saunders, Jr, *J. Am. Chem. Soc.* **116**, 5400–5404 (1994). (b) W. H. Saunders, Jr and J. E. Van Verth, *J. Org. Chem.* **60**, 3452–3458 (1995).
7. J. Li and W. Wu, *Theor. Chim. Acta* **89**, 105 (1994).
8. P. C. Hiberty and D. L. Cooper, *J. Mol. Struct. (THEOCHEM)* **169**, 437–446 (1988).
9. S. Shaik and P. C. Hiberty, *Adv. Quantum Chem.* **26**, 99–163 (1995).