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Short Communication

Intrinsic barriers for imbalanced versus balanced transition structures

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ABSTRACT: *Ab initio* calculations were carried out on the identity gas-phase proton and methyl cation transfers from carbon acids (acetaldehyde and propene) to conjugate bases (acetaldehyde enolate and allyl anions) at the MP2/6–311+G**//MP2/6–311+G** level. The percentage bond length changes at the transition structure (TS) show that in the imbalanced TS the exoergic bond contraction is always ahead of the proton transfer and concurrent endoergic bond stretching with a net gain of resonance stabilization. This is achieved by a lag in charge delocalization into the π-acceptor group in the TS. The reaction through an imbalanced TS is in accord with a basic natural law of the minimum energy path in physical or chemical changes. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculation; identity proton and methyl cation transfer; principle of non-perfect synchronization; imbalanced transition structure; resonance stabilization

INTRODUCTION

There has been considerable interest in the study of the imbalanced transition state in which various processes such as bond formation and bond cleavage, development or destruction of charge and π-overlap (resonance) and solvation/desolvation have made unequal progress or have developed non-synchronously.[1] An understanding of these imbalances and their origin is important because transition state imbalances are known to cause elevation of intrinsic barriers ($\Delta E_0^{\ddagger}$) or lower intrinsic rate constants (k_0).[1] According to the principle of non-perfect synchronization (PNS) proposed by Bernasconi,[1] a product stabilizing factor that develops late along the reaction coordinate or a reactant stabilizing factor that is lost early lowers k_0. Hence the lack of synchronization between proton transfer and charge delocalization (the lag in charge delocalization) in the deprotonation of carbon acids activated by π-acceptors causes little development of resonance stabilization of the transition state, which is considered the major reason why reactions that lead to resonance-stabilized products have high intrinsic barriers. The lag in resonance development is therefore considered to create a high barrier than would prevail if this resonance were developed synchronously with proton or charge transfer. This is, however, in apparent contradiction to a basic law of nature that physical or chemical changes should occur always through a minimum energy path.

In an effort to resolve this problem, Bernasconi and co-workers[2] and Saunders and Van Verth[3] carried out high-level *ab initio* calculations on several typical gas-phase identity proton transfers, *e.g.*

$$\mathrm{O\overset{\scriptscriptstyle ---}{-}CH\overset{\scriptscriptstyle ---}{-}CH_2^- + CH_3CHO \rightleftharpoons CH_3CHO + O\overset{\scriptscriptstyle ---}{-}CH\overset{\scriptscriptstyle ---}{-}CH_2^-} \qquad (1)$$

$$\mathrm{CH_2\overset{\scriptscriptstyle ---}{-}CH\overset{\scriptscriptstyle ---}{-}CH_2^- + CH_3CH{=}CH_2 \rightleftharpoons CH_3CH{=}CH_2 + CH_2\overset{\scriptscriptstyle ---}{-}CH\overset{\scriptscriptstyle ---}{-}CH_2^-} \qquad (2)$$

In their work, they focused on the transition state *charge* imbalances and one of their conclusions reads, ‘the transition state imbalances do not lead to a significant increase in the intrinsic gas phase barriers (in fact there is a slight decrease).’ They attributed it to a very strong influence of inductive/field and electrostatic/hydrogen bonding effects on the gas-phase intrinsic barrier.[1c]

In this work, we aimed to show that the imbalanced transition structure (TS) actually has a lower intrinsic barrier than a hypothetical TS that has a synchronously developed resonance or balanced TS. We approach the imbalance problem through bond length (or bond order) changes involved on going to the TS from the separated reactants using the identity gas-phase proton transfer processes [Eqns (1) and (2)] and the corresponding

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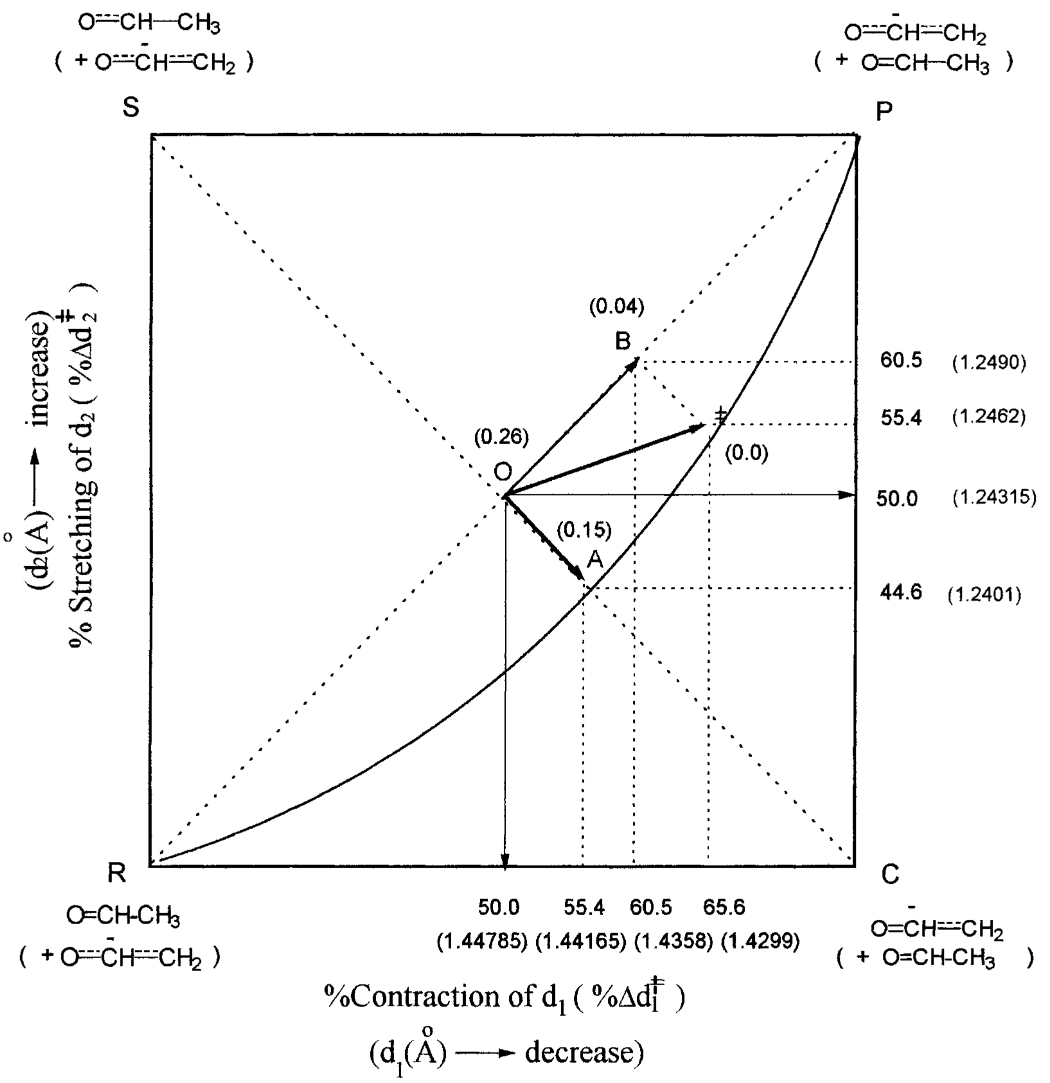


Figure 1. More O'Ferrall–Jencks diagram for gas-phase identity proton transfer from acetaldehyde to enolate anion. The S (stretched) and C (contracted) corners represent hypothetical states of d_2 stretched and d_1 contracted to their respective length in the enolate. The relative $\Delta E^{\ddagger}$ values in kcal mol^{-1} are shown in parentheses; $\%\Delta d^{\ddagger} = [(d^{\ddagger} - d_R)/(d_P - d_R)] \times 100$. The energy at the TS (‡) is −306.29960 hartree with an intrinsic barrier height $\Delta E_0^{\ddagger} = 0.21$ kcal mol^{-1}

methyl cation transfers:

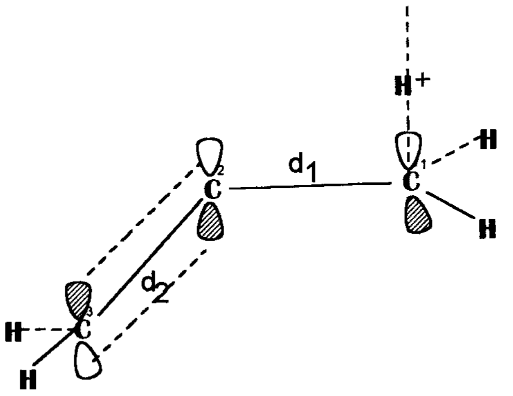
$$\mathrm{O{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2^- + CH_3CH_2CHO \rightleftharpoons CH_3CH_2CHO + O{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2^-} \qquad (3)$$

$$\mathrm{CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2^- + CH_3CH_2CH{=}CH_2 \rightleftharpoons CH_3CH_2CH{=}CH_2 + CH_2{\overset{\cdots}{-}}CH{\overset{\cdots}{-}}CH_2^-} \qquad (4)$$

in which there is 50% proton and methyl cation transfer in the TS.

The *ab initio* calculations were carried out on reactions 1–4 at the MP2/6–311+G**//MP2/6–311+G** level. We chose this approach because the dominant factor determining intrinsic barrier heights ($\Delta E_0^{\ddagger}$) in transfer reactions is the extent of structural reorganization that occurs upon passage from reactants to TS.[4] A bond stretch associated with a hybridization change from sp^2 to sp^3 should cost energy (an endoergic process), leading to an enhanced barrier height, in contrast to a bond contraction associated with a rehybridization from sp^3 to sp^2 (an exoergic process). Bond length changes required to achieve the TS are known to be linearly correlated with the intrinsic barriers.[4]

The reactions studied, Eqns (1)–(4), are identity carbon-to-carbon proton and methyl cation transfers so that the activation energy represents the intrinsic barrier, $\Delta E_0^{\ddagger}$. At the TS, the proton and methyl cation are transferred 50.0%, *i.e.* the proton and methyl cation being transferred are located at equal distances from the two identical groups. For example, we calculated the intrinsic barriers, $\Delta E_0^{\ddagger}$, for the fully optimized imbalanced TS (*cis-gauche* form) of reaction 1 at point ‡ $\{E^{\ddagger} = -306.29960$ hartree; $\Delta E_0^{\ddagger} = 0.21$ kcal mol^{-1} (1 kcal = 4.184 kJ);



Scheme 1

$\%\Delta d^{\ddagger}_{1}/\%\Delta d^{\ddagger}_{2} = 65.6/55.4$, where $\%\Delta d^{\ddagger} = [(d^{\ddagger} - d_{R})/(d_{P} - d_{R})] \times 100\}$, and for the hypothetical transition structures at points O (= 50.0/50.0), A (= 55.4/44.6) and B (= 60.5/60.5) and the relative $\Delta E^{\ddagger}_{0}$ values are shown in parentheses on the More O'Ferrall–Jencks diagram[5] in Fig. 1. The diagram is meant only to illustrate qualitatively the reactions as they relate to the transition structures by percentage bond length changes and hence it is not in proper scale. The upper two corners, **P** (product) and **S** (stretched form), are destabilized due to the C=O stretching so that the hypothetical balanced TS at O shifts to points A and B, leading to the resultant optimized TS at point ‡. It must be stressed that all four points on the diagram represent 50% proton transfer, or reaction progress, since we kept the two $H^{+}\cdots$enolate distances equal in all cases. We note that all supposedly balanced TSs, O, A and B, have higher intrinsic barriers than the imbalanced TS (‡), even though the differences in $\Delta E^{\ddagger}_{0}$ are small (0.04–0.26 kcal mol^{-1}). This means that the imbalanced TS is actually the most resonance-stabilized form, and the imbalance does not cause elevation of the intrinsic barrier or lower the intrinsic reaction rate as has been believed or predicted based on the imbalanced charge transfers.[1] Hence the TS imbalance in the gas phase does not contradict a basic natural law of the minimum potential energy path for physical or chemical changes.

A similar diagram for reaction 2 ($E^{\ddagger} = -234.44781$ hartree and $\Delta E^{\ddagger}_{0} = 4.74$ kcal mol^{-1}, for the *cis-gauche* form) was obtained (not shown) with the same behavior regarding the correlation between the TS structure and $\Delta E^{\ddagger}_{0}$ [$\delta\ \Delta E^{\ddagger}_{0} = \Delta E^{\ddagger}_{0}$ (50/50) $-\ \Delta E^{\ddagger}_{0}$ (55/47) = 0.03 kcal mol^{-1}] with that for reaction 1. The only difference is the length of vector **O‡,** which should represent the size or extent of the imbalance. The imbalance parameters, **O‡,** determined for various π-acceptor groups Y (CH_3—Y/CH=Y^{-}) decrease in the order NO_2 (8.0)[2c] ≥CH=O (7.8) > CH=CH (6.2) ≥ C=N (5.9).[5b]

Identical diagrams for methyl cation transfers, Eqns (3) and (4), were obtained (not shown) with the more stable imbalanced than the balanced TS [$\delta\ \Delta E^{\ddagger}_{0} = \Delta E^{\ddagger}_{0}$ (50/50) $-\ \Delta E^{\ddagger}_{0}$ (72/57) = 0.58 kcal mol^{-1} and $\delta\ \Delta E^{\ddagger}_{0} = \Delta E^{\ddagger}_{0}$ (50/50) $-\ \Delta E^{\ddagger}_{0}$ (67/53) = 0.25 kcal mol^{-1} for Eqns (3) and (4), respectively].

WHAT IS THE REAL NATURE OF THE IMBALANCED TS?

The developing electron pair on C-1 in the TS (at 50% deprotonation) in Scheme 1 should have 50% lone pair (n) character. It is well known that the n–π* first-neighbor vicinal (n → $\pi_{2,3}$*) interaction provides the greatest contribution to the second-order charge delocalization.[6] In such a process, the vicinal $\pi_{2,3}$ bond is partially lost while a geminal $\pi_{1,2}$ bond is partially formed.[6,7] It is obvious that at 50% proton transfer the first neighbor vicinal delocalization of the charge created (50%) at C-1 can only take place partially, most probably less than 50%, to $\pi_{2,3}$ owing to a low degree of vicinal n–π* overlap (this is in line with the qualitative explanation for charge imbalance offerred by Kresge:[8] the charge on d_2 at the TS is small since it is a fraction of a fraction). This is the reason why there is an imbalance in the charge transfer advocated by Bernasconi and co-workers.[1–3]

On the other hand, however, π bond formation between C-1 and C-2 is an exoergic process, whereas the concerted but asynchronous bond cleavage of the $\pi_{2,3}$ bond is an endoergic process. Therefore, the formation of the $\pi_{1,2}$ bond is actually 'paying for' the concurrent breaking of the $\pi_{2,3}$ bond, and in order to conserve the resonance stabilization energy, or π-bond-order,[9] the exoergic $\pi_{1,2}$ formation (with resonance energy gain) should proceed ahead of, or should be greater than, the proton transfer (50%) and also of the endoergic $\pi_{2,3}$ bond cleavage (with resonance energy loss).

This is why the $\%\Delta d^{\ddagger}_{1}$ is always greater than 50% (% proton transfer) and $\%\Delta d^{\ddagger}_{2}$ in the imbalanced TS.[2,3] Hence there is actually a net gain in the resonance energy by proceeding through the *imbalanced TS*, and the intrinsic barrier is lower, not higher, than *the balanced TS*. The extra n → π* resonance stabilization of *ca* 0.3 kcal mol^{-1} for the imbalanced TS (‡) compared with the balanced TS (O) corresponds to a greater charge transfer of *ca* 0.0005 e from the developing electron pair (n) to the vicinal $\pi_{2,3}$* orbital.[6c,,7a] The experimentally observed decrease in the intrinsic rate in solution should reflect the lag in solvation of the negative charge on the acceptor π group in the TS, which should enhance the intrinsic barrier.

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