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Resonance Effect in the Allyl Cation and Anion: A Revisit

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The interest over the magnitude of the conjugation effect in the allyl cation (**1**) and anion (**2**) has been revived recently by Barbour and Karty (*J. Org. Chem.* **2004**, *69*, 648−654), who derived the resonance energies of 20−22 and 17−18 kcal/mol for **1** and **2**, respectively, using an empirical extrapolation approximation. This paper revisits the case by explicitly calculating the Pauling−Wheland resonance energy, which measures the stabilization from the most stable resonance structure to the delocalized energy-minimum state of a conjugated system, using our newly developed block-localized wave function (BLW) method. This BLW method has the geometrical optimization capability. The computations result in adiabatic resonance energies of 37 kcal/mol for **1** and 38 kcal/mol for **2**. The significant disagreement between these values and Barbour and Karty's results originates from the neglect of structural and electronic variations in their derivation which are energy costing.

Although theoretically the resonance effect has been well-established based on the resonance theory,[1,2] i.e., the resonance energy is the energy change from the most stable resonance structure to the delocalized energy minimum state of a conjugated system, the computational and experimental quantification has been proved to be difficult. Indirectly, numerous schemes have been designed to measure the resonance effect. An often-employed approximation is to rotate a part of the system to deactivate the conjugation effect over the rotated bond, and the subsequent energy variation (rotation barrier) is attributed to the resonance stabilization energy.[3,4] However, with the quenching of the conjugation effect in the process of rotation, other factors such as hyperconjugative stabilization, steric strain, etc. are introduced and ultimately complicate the interpretation of the rotation barrier. Notably, Daudey et al. probed both the conjugation effect in the planar structure and the hyperconjugation effect in the perpendicular structure of butadiene by means of substituting the π molecular orbitals (MO's) with the ethylenic π orbital obtained at the same level with the same basis set and clearly demonstrated that the small rotation barrier around the central carbon−carbon bond as well as the negligible central bond length variation originate from the cancellation between the conjugation and hyperconjugation effects which are comparable in magnitude.[5] Similarly, our recent detailed analysis of the rotation barriers in formamide and its likes showed that the conjugation stabilization energies in planar conformations are consistently higher than the rotation barriers (ranges from 4.5 to 22.8 kcal/mol) by 10−15 kcal/mol, mostly due to the offset of the hyperconjugation effect in the perpendicular conformations.[6] Another frequently adopted approach to estimate the conjugation stabilization is the design of isodesmic reactions.[7] For instance, the resonance effect in butadiene can be measured by the following reaction

$$CH_2{=}CH{-}CH{=}CH_2 + 2CH_3CH_3 \rightarrow CH_3CH_2CH_2CH_3 + 2CH_2{=}CH_2 \quad (1)$$

where the experimental enthalpy change is 8.5 kcal/mol.[8] However, it has been recognized that the stabilization energies for the same system may not be unique and depend on the selection of reference molecules, where additional effects such as strain, conjugation, and hyperconjugation may significantly contribute to the overall reaction enthalpy and are hard to screen out.[9] For example, if the following isodesmic reaction is used

$$CH_2{=}CH{-}CH{=}CH_2 + 2CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + 2CH_2{=}CHCH_3 \quad (2)$$

we will find the "resonance" energy in butadiene to be only 3.1 kcal/mol, apparently due to the omission of

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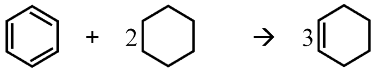
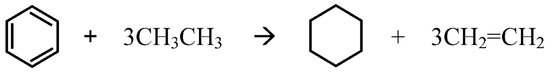
the hyperconjugation effect in the propylene. The most well-known case in this regard is benzene, and a wide range of computed resonance energy can be found in the literature,[10] although experimentally the resonance stabilization energy (36 kcal/mol) is based on the following homodesmotic reaction



(3)

However, we must remember that there is nontrivial hyperconjugative interaction from the adjacent methylene groups to the double bond in cyclohexene. In other words, the above reaction underestimates the resonance stability in benzene if the hyperconjugation in cyclohexene is not appropriately considered.[11] A value of 48 kcal/mol can be derived based on the following reaction.



(4)

Examples of significant controversies over the magnitude of the resonance effect are the allyl cation (**1**) and anion (**2**) (Scheme 1).[3,12−14] Wiberg and co-workers initially concluded that the cation had significant resonance stabilization whereas the anion had little stabilization,[3] but Gobbi and Frenking found that the conjugation effects in both ions are comparable in magnitude based on the topological analysis of the electron density distribution and the natural bond orbital (NBO) partitioning scheme.[12]

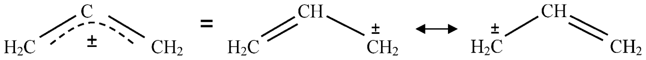
$CH_2{=}CH{-}CH_2^+$

1

$CH_2{=}CH{-}CH_2^-$

2

SCHEME 1



An appropriate method to quantitatively measure the resonance effect should be the ab initio valence bond (VB) theory,[15] where a delocalized system is described by a few resonance structures and each resonance structure is mathematically expressed by a Heitler−London−Slater−Pauling (HLSP) function. As a consequence, the conventional Pauling−Wheland resonance energy can be well defined and computed. Our earlier VB calculations quantitatively supported Gobbi and Frenking's above conclusions.[13] In these computations, we froze the σ MO's to reduce the computational costs and derived the vertical resonance energy (VRE), which is the energy difference between the most stable resonance structure and the delocalized state at the same optimal delocalized state geometry: 55.7 kcal/mol in **1** and 52.3 kcal/mol in **2** with the 6-31G(d) basis set. These results were later refined by the block-localized wave function (BLW) method,[16,17] which combines the advantages of both the VB and MO theories and relaxes the σ MO's self-consistently. The BLW method results in the VRE's in **1** and **2** as 45.7−44.7 kcal/mol and 46.7−48.2 kcal/mol, respectively.[16] The new data highlight the importance of electronic relaxation for the σ frame.

Most recently, Barbour and Karty revived the interest over the resonance effect in the allyl ions by examining the following isodesmic reactions[14]

$$CH_2{=}CH{-}CH_3 + CH_3CH_2CH_2^{\pm} \rightarrow CH_2{=}CH{-}CH_2^{\pm} + CH_3CH_2CH_3 \quad (5)$$

On the basis of a crude extrapolation technique, they decomposed the reaction enthalpies (15.2−15.7 and 26.7−25.6 kcal/mol) in terms of resonance and induction and finally derived the resonance energies of 20−22 and 17−18 kcal/mol for the allyl cation and anion, respectively. However, remarkable structural and electronic differences in the terminal methylene groups in $CH_3CH_2CH_2^{\pm}$ and $CH_2{=}CH{-}CH_2^{\pm}$ are neglected and unaccounted for in Barbour and Karty's analyses and in our opinion, this omission is the prime reason for the gap between the two sets of data derived in our method and their approach.

We argue that a stringent and quantitative measurement of the resonance effect cannot avoid the usage of localized and nonorthogonal orbitals as in the VB theory where the concept of resonance and the resonance theory were originally founded. The recently accomplished geometrical optimization capability of the BLW method[18] based on Gianinetti et al.'s algorithm[19] and ported to the GAMESS software[20] spurs us to revisit the resonance effect in the allyl ions by optimizing the geometries of individual resonance structures and derive the adiabatic resonance energy (ARE, or theoretical resonance energy TRE as previously called[10f]), which is the energy difference between the optimal resonance structure and the

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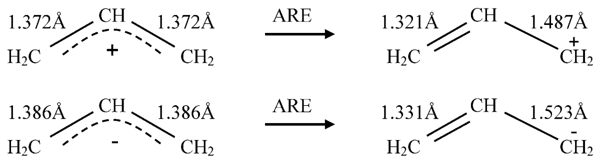


FIGURE 1. Illustrations of the definition of adiabatic resonance energy (ARE) in the allyl ions. Data are from the HF (left side) and BLW (right wide) optimizations with the 6-311+G(d,p) basis set.

TABLE 1. Optimal Carbon−Carbon Bond Lengths (Å) in Delocalized and Localized Structures

allyl ion	basis set	delocalized structure	localized structure	
		R(CC)	*R*(C=C)	*R*(C−C)
$C_3H_5^+$	6-31G(d)	1.373	1.321	1.486
	6-31+G(d)	1.374	1.323	1.487
	6-311+G(d,p)	1.372	1.321	1.487
$C_3H_5^-$	6-31G(d,p)	1.382	1.331	1.497
	6-31+G(d)	1.388	1.332	1.521
	6-311+G(d,p)	1.386	1.331	1.523

TABLE 2. Computed Resonance Energies (kcal/mol) in Allyl Ions

allyl ion	basis set	VRE	ARE
$C_3H_5^+$	6-31G(d)	45.7	37.8
	6-31+G(d)	44.7	36.9
	6-311+G(d,p)	44.3	36.6
$C_3H_5^-$	6-31G(d,p)	46.7	39.0
	6-31+G(d)	48.2	38.8
	6-311+G(d,p)	47.6	38.1

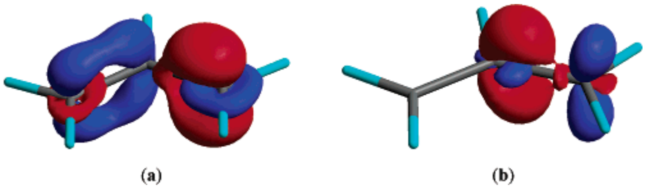

(a) (b)

FIGURE 2. Electron density difference (EDD) maps for the allyl ions (isodensity = 0.01 au, with red denoting the electron gain and blue denoting the electron loss): (a) allyl cation and (b) allyl anion.

optimal delocalized energy minimum state (Figure 1). The energy minimum (delocalized) state is represented by a HF wave function and the most stable resonance (localized) structure is represented by a BLW.

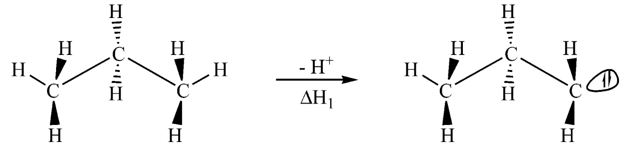
Table 1 compiled the optimal structural parameters for the delocalized and localized allyl ions with the basis sets of 6-31G(d), 6-31+G(d), and 6-311+G(d,p), while both VRE's and ARE's are listed in Table 2. In the delocalized energy minimum state, which is contributed by two equivalent resonance structures (Scheme 1), both allyl ions adopt a C_{2v} symmetry and the carbon−carbon bond lengths are 1.37 Å for **1** and 1.39 Å for **2**. With the localization of the positive/negative charge in a terminal carbon, the double bonds shorten by about 0.05 Å to 1.32 Å for **1** and 1.33 Å for **2**, which are comparable to the double bond length in ethylene (1.317−1.321 Å with the same basis sets at the HF level). For the single Csp^2−Csp^2 bond length, discrepancy exists simply due to the different strengths of steric repulsions. Steric strain is typically comprised of electrostatic and Pauli exchange interactions. In the localized allyl cation, the single carbon−carbon bond length is about 1.49Å, irrespective of the basis sets. In the localized allyl anion, however, optimization with the 6-31G(d) basis set results in a value of 1.50Å, while the addition of a diffuse function lengthens the single Csp^2-Csp^2 bond length to 1.52Å. Further enlargement of the basis set does not vary the geometrical parameters noticeably. This is in accord with the generic knowledge that diffuse functions are critical to the computations of anions. As a matter of fact, the single Csp^2-Csp^2 bond length in the allyl anion **2** is very close to those in the optimal Kekulé structure (1.517−1.522Å[11]) but shorter than that in the allyl cation **1** due to the reduced eclipsed repulsion as the vertical *p* orbital in the terminal carbon is vacant in **1** but doubly occupied in **2**.

Although structural differences between the two allyl ions are apparent, their resonance energies are nevertheless of the same magnitude and differ by only about 2 kcal/mol, and show little basis set dependency (Table 2). Our BLW computations reveal that the ARE's in the allyl cation (**1**) and anion (**2**) are about 37 and 38 kcal/mol, respectively. This resonance capability is significantly stronger than neutral systems of comparable size, such as butadiene. In the case of butadiene, our computed ARE is 9.2−9.9 kcal/mol, which is in good agreement with the experimental estimation (8.5 kcal/mol). We have pointed out that the equal distribution of the charge (no matter whether it is positive or negative) across the system is the driving force for the very high and comparable resonance energies in the allyl ions.[13,16] The accumulation of charges in one part of a system may significantly destabilize the system after all, and thus is strongly disfavored.

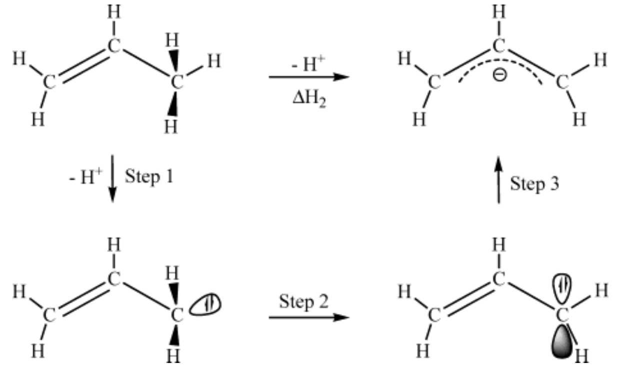
Figure 2 plots the electron density difference between the localized and delocalized states, and shows the charge migration from the most stable resonance structure to the delocalized energy minimum state in the allyl ions. Interestingly, in the allyl cation, the two carbon atoms forming the carbon−carbon double bond equally lose π electrons to the positively charged carbon, with a small reverse polarization effect in the σ frame from one end to the other. In the allyl anion, however, the electron migration essentially occurs between the negatively charged carbon and its adjacent carbon, with the former donating electrons to the latter. This comes from the fact that the double bond in the localized allyl anion has already remarkably polarized toward the other end due to the steric repulsion between the lone pair in the negatively charged carbon and the π bond.[16]

The above BLW computations and discussion provide a rational picture for the resonance effect in both allyl ions, which are consistent with our other calculations.[6,11,16,18] Why then Barbour and Karty derived much low resonance stabilizations and how to understand the big gap between our current data (37 kcal/mol for **1** and 38 kcal/mol for **2**) and Barbour and Karty's (20−22 kcal/mol for **1** and 17−18 kcal/mol for **2**) which differ by as high as about 20 kcal/mol? Although Barbour and Karty used an empirical approach to estimate the resonance stability in the allyl ions, their arguments are essentially established on the experimental findings that propene is more acidic than propane by 25.6 kcal/mol in the gas phase, which "should roughly correspond to the upper bound for the resonance energy in the allyl anion".[14]

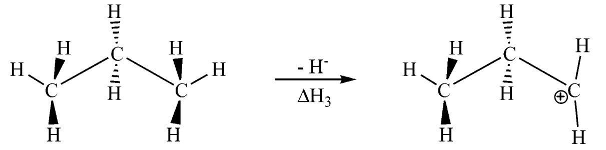
SCHEME 2



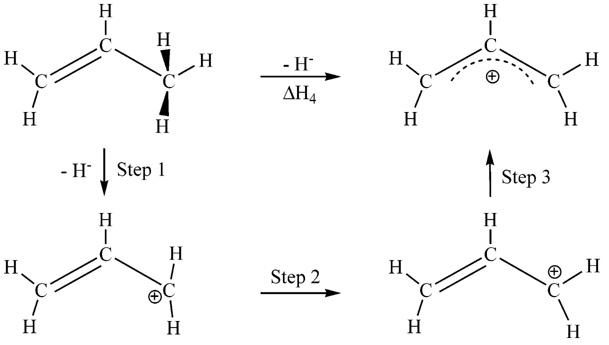
SCHEME 3



SCHEME 4



SCHEME 5



However, remarkable structural and electronic changes for propene with the proton abstraction which do not exist for propane are simply neglected. Scheme 2 shows the deprotonation process of propane with the reaction enthalpy ΔH_1. With the proton abstraction, the terminal carbon retains its sp^3 hybridization mode and accommodates the lone pair in one hybrid orbital, which is in the staggered position with respect to the ethyl group to reduce the steric repulsion.

In sharp contrast, the deprotonation of propene to the allyl anion with the reaction enthalpy ΔH_2 consists of three successive steps as illustrated in Scheme 3. The first step is similar to propane and the enthalpy change is $\Delta H_1 + \Delta E_{\text{ind}}$ where ΔE_{ind} is the inductive effect due to the vinyl group. The last step refers to the conjugation of the lone pair with a double bond, which is the focus of our studies. It is the second step that is primarily responsible for the discrepancy between our data and Barbour and Karty's. This step will consume a considerable amount of energy as it is composed of the following four changes: (1) the deactivation of the hyperconjugative interaction between the terminal CH_2 group and the π part of the double bond, which is comparable to the hyperconjugation effect in propene whose strength is about 5 kcal/mol;[16] (2) the deactivation of the negative hyperconjugation from the lone pair in the methylene group to the ethyl group, which stabilizes the system by about 12.8 ± 0.4 kcal/mol based on the BLW calculations of $CH_3CH_2CH_2^-$ where the methylene group is rotated and flattened with the same three basis sets employed in this work; (3) the steric strain due to the rotation of the methylene group from the staggered position to the eclipsed position, whose magnitude should be close to the rotation barrier in ethane (~3 kcal/mol[17b]); and (4) the flattening of the methylene group, which could be evaluated by using the methane anion CH_3^- as a model (2.4 kcal/mol at the B3LYP/6-311+G(d,p) level). Thus, the overall energy cost in step 2 is $5.0 + 12.8 + 3 + 2.4 = 23.2$ kcal/mol. Summing all the three steps together, we get $\Delta H_2 = \Delta H_1 + \Delta E_{\text{ind}} + 23.2 - \text{ARE}$. If we use the experimental data $\Delta H_2 - \Delta H_1 = -25.6$ kcal/mol, and Barbour and Karty's result $\Delta E_{\text{ind}} = -9.5$ kcal/mol, we finally get the approximate resonance stabilization of 39 kcal/mol in the allyl anion. This is in accord with our quantum mechanical BLW computations which generate the adiabatic resonance energy of 38 kcal/mol for the allyl anion. This value is also close to the resonance energy in the formate anion of 40 kcal/mol obtained by Hiberty and Byrman[21] (or 42 kcal/mol with the BLW method and 6-311+G(d,p) basis set).

A similar analysis on the allyl cation can be made based on Schemes 4 and 5. Notably, the hydride abstraction of propane with the reaction enthalpy ΔH_3 leads to the terminal planar methylene group perpendicular to the CCC plane, while the hydride abstraction of propene to the allyl cation with the reaction enthalpy ΔH_4 also consists of three successive steps. The enthalpy changes for the first and third steps in Scheme 5 are $\Delta H_3 + \Delta E_{\text{ind}}$ and ARE, respectively, and the second step consists of three changes: (1) the deactivation of the hyperconjugative interaction between the terminal CH_2 group and the π part of the double bond (about 5 kcal/mol); (2) the deactivation of the positive hyperconjugation from the ethyl group to the vacant p orbital on the terminal carbon, whose strength can be computed by the BLW method, which is 13.2 kcal/mol with the 6-311+G(d,p) basis set; and (3) the steric strain due to the rotation of the methylene group from the staggered position to the eclipsed position, whose magnitude is close to zero. Summing them up, we get the overall energy costs of 18.2 kcal/mol in the step 2, and $\Delta H_4 = \Delta H_3 + \Delta E_{\text{ind}} + 18.2 - \text{ARE}$. Since the experimental data $\Delta H_4 - \Delta H_3 = -15.7$ kcal/mol, and Barbour and Karty's result $\Delta E_{\text{ind}} = 4.4$ kcal/mol, we derive the approximate resonance stabilization of 38 kcal/mol in the allyl cation.

One final note is that Barbour and Karty mistook the energy difference of localized states of formic acid and anion (375.5 kcal/mol) instead of the energy difference of delocalized states of formic acid and anion (352.9 kcal/mol) from Hiberty and Byrman's work[21] to compare the experimental acidity of formic acid (345 kcal/mol) and question the accuracy of the ab initio VB calculations.

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[21] Hiberty, P. C.; Byrman, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 9875−9880.

The discrepancy between the above two energy differences (375.5 vs 352.9 kcal/mol) actually reflects the resonance contribution to the acidity of formic acid, while the difference between the computed (352.9 kcal/mol) and the experimental (345 kcal/mol) acidities highlights the error of the HF method and the necessity to take the electron correlation into account to obtain accurate computed acidities.

In conclusion, our BLW computations with various basis sets consistently confirm the similarity of the conjugation effect in the allyl cation (**1**) and anion (**2**), with the adiabatic resonance energy, which measures the stabilization energy from the most stable resonance structure to the optimal delocalized energy minimum state, 37 kcal/mol for **1** and 38 kcal/mol for **2**. The underestimation of the resonance effect by Barbour and Karty comes from the neglect of the structural evolutions with the proton and hydride abstractions at the methyl group in propene which are energy-demanding but will be offset by the strong resonance stabilization in the allyl ions.

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Supporting Information Available: Cartesian coordinates and total electronic energies for the delocalized (the energy minimum states) and localized (the most stable resonance structures) structures of the allyl ions are summarized. This material is available free of charge via the Internet at http://pubs.acs.org.

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