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Resonance Energies of the Allyl Cation and Allyl Anion: Contribution by Resonance and Inductive Effects toward the Acidity and Hydride Abstraction Enthalpy of Propene

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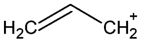
Density functional theory was employed to calculate the acidities and hydride abstraction enthalpies of propene (**3**) and propane (**4**), along with their vinylogues (**5** and **6**, respectively). The same reaction enthalpies were calculated for the propene vinylogues in which the terminal vinyl group was rotated perpendicular to the rest of the conjugated system (**7**). The contribution by resonance and inductive effects toward the acidity and hydride abstraction enthalpy of each vinylogue of **5** ($n = 1-3$) was computed and extrapolated to $n = 0$ (the parent propene system). The resonance energies of the allyl cation and anion were determined to be about 20−22 and 17−18 kcal/mol, respectively. Comparisons are made to resonance energies calculated using other methodologies.

Introduction

Determining the resonance energy in a molecular species is nontrivial.[1] This is exemplified by the debate in recent literature regarding the resonance energy in the allyl cation (**1**) and in the allyl anion (**2**). Wiberg et al.[2] suggested, based on the significantly smaller calculated rotational barrier of the methylene group in **2**, i.e. 19 kcal/mol, than in **1**, i.e., 36 kcal/mol, that there is significant resonance energy in **1**, but comparatively little in **2**. On the contrary, Gobbi and Frenking[1] suggested that the resonance energy in **1** and **2** are of about the same magnitude. Their conclusions were based on examining the changes in energy and electronic structure of **1** and **2** upon rotation of the CH_2 group and upon selected other molecular distortions. Mo et al.[3] provided evidence that was in qualitative agreement with Gobbi and Frenking. However, their calculated resonance energies (55.7 kcal/mol for **1** and 52.3 kcal for **2**) were much larger than the respective methylene rotational energies. To account for this, they suggested that the rotational transition state was heavily stabilized through hyperconjugation. Furthermore, they argued that the smaller rotational barrier of **2** than that of **1** is largely due to the relaxation of the geometry of the methylene carbon in **2** from planar in the fully optimized structure to pyramidal in the rotational transition state. On the other hand, there is little geometry change about the methylene carbon in the rotational transition state of **1**. Mo and Peyerimhoff[4] came to similar qualitative conclusions, with slightly different values, suggesting that the resonance energy in the cation and anion are 46 and 47 kcal/mol, respectively. Rablen's results,[5] however, suggest that the resonance energy in the 2-methylallyl anion is about 23 kcal/mol.



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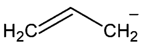

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Several of the aforementioned studies intimately involve the energy barriers to rotation of the CH_2 group. As pointed out by Mo and Peyerimhoff,[4] as well as by Mo et al.,[3] the change in energy between the rotational transition state and the fully optimized geometries of the allyl ions can be broken down into 4 distinct interaction energies: (1) π resonance energy, (2) steric interactions, (3) hyperconjugation, and (4) geometry relaxation. Consequently, it may be difficult to extract only the resonance energy by examining the energy changes accompanying the methylene rotation in allyl and distorted allyl ionic systems. Therefore, Mo and Peyerimhoff[4] and Mo et al.[3] used localized wave functions to calculate the energies of individual resonance structures, effectively being able to turn off conjugation and hyperconjugation effects independently. The result of this approach was the quantification of the contribution by each of the above four interactions toward the rotational barrier in each allyl system.

In this paper, we use an approach that has previously been applied toward determining the resonance versus inductive effects in the enhanced acidity of formic acid over methanol.[6] Rather than focusing strictly on the energetics of the allyl cation and anion, we focus on reaction thermochemistries involving these ions. Specif-

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[1] Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275.
[2] Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61−72.
[3] Mo, Y.; Zhenyang, L.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1996**, *100*, 6469.
[4] Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687.
[5] Rablen, P. R. *J. Am. Chem. Soc.* **2000**, *122*, 357−368.
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ically, we focus on proton abstraction and hydride abstraction at the methyl group in propene (eqs 1 and 2)

$$H_2C{=}CH{-}CH_3 \rightarrow H_2C{=}CH{-}CH_2^- + H^+ \quad (1)$$

$$H_2C{=}CH{-}CH_3 \rightarrow H_2C{=}CH{-}CH_2^+ + H^- \quad (2)$$

in order to study the resonance energy in the allyl anion and cation, respectively. We then compare the resulting acidity ($\Delta_{acid}H°$) and hydride abstraction enthalpy ($\Delta_{HA}H°$) of propene with the acidity and hydride abstraction enthalpy at the terminal carbon of propane (eqs 3 and 4).

$$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2^- + H^+ \quad (3)$$

$$CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2^+ + H^- \quad (4)$$

The difference in acidity between propene and propane (eqs 1 and 3) is taken to be due mainly to resonance and inductive effects provided by the vinyl group (see Methodology and Discussion). Similarly, the difference in hydride abstraction enthalpy between propene and propane (eqs 2 and 4) is taken to be due mainly to resonance and induction. Using our methodology outlined below, we can then separate the contribution by inductive effects from the contribution by resonance toward these differences in reaction enthalpy.

Our results indicate that the resonance energy of the allyl cation is about 20−22 kcal/mol, and that of the anion is about 17−18 kcal/mol. These results are in qualitative agreement with Gobbi and Frenking,[1] Mo and Peyerimhoff,[4] and Mo et al.,[3] demonstrating that there is significant resonance stabilization in both the cation and the anion of about the same magnitude. However, the resonance energies that we calculate are significantly less than those calculated by Mo and Peyerimhoff[4] and by Mo et al.[3] Additionally, our results suggest that there are significant inductive effects provided by the vinyl group in the allyl ions, which serve to stabilize the anion while destabilizing the cation.

Methodology

To study the resonance energy in the allyl anion, we examine the acidity enhancement of propene (**3**) relative to propane (**4**). Because the CH_3CH_2 group does not contribute significantly via induction (there are no significantly electronegative atoms) and does not contribute via resonance, this acidity difference is taken to largely be the sum of inductive and resonance effects provided by the vinyl group in **2** and **3**. Given that resonance is not active in **3**, the total resonance contribution toward the acidity enhancement of **3** over **4** is taken to be the resonance energy in **2**.

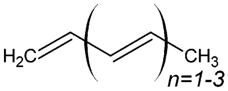
$H_2C{=}CH{-}CH_3$

3

$CH_3CH_2CH_3$

4

The acidities of the $n = 1-3$ vinylogues of propene and propane (**5** and **6**, respectively) are also examined. Any residual acidity difference between **5** and **6** must still be due largely to the resonance and inductive effects of the terminal vinyl group in **5** (and its anion) not present in **6** (and its anion). It is clear that the inductive effect of the terminal vinyl group on the acidity of the methyl proton is attenuated in **5** relative to that in **3**, due to the increased separation. Likewise, as a result of the greater importance of added resonance in the anion of **6** (compared to that in **4**) than in the anion of **5** (compared to **3**), we would expect that the resonance contribution toward the acidity difference between **5** and **6** should be less than that between **3** and **4** and should decrease with n.[7]



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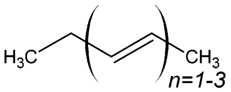

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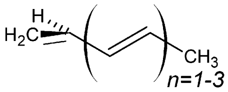

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To separate out the contribution by resonance and inductive effects toward the acidity difference between **5** and **6**, we also examine the acidity of the $n = 1-3$ propene vinylogues in which the terminal vinyl group is perpendicular to the rest of the conjugated system (**7**). The motivation for this is that resonance should not be active in **7**, whereas the inductive effect of the terminal vinyl group should remain unchanged; the distance between the terminal vinyl group and the methyl group is essentially the same in **5** and **7**. Therefore, the acidity difference between **5** and **7** is taken to be the result of only the resonance contribution provided by the terminal vinyl group. Likewise, the acidity difference between **6** and **7** is taken to be the result of only the inductive contribution by the terminal vinyl group. Extrapolation of the resonance and inductive contributions in the vinylogues of propene to $n = 0$ yields the resonance and inductive contributions provided by the vinyl group in the parent propene system.

One advantage of employing this methodology to studying resonance in the allyl anion is that the steric contribution toward the energy of rotation of the methylene group in the allyl anion is essentially filtered out. This is because the geometries are nearly identical in both the reactant and the product of each vinylogue species we examine. Steric effects should therefore contribute little toward acidities, and even less toward acidity differences.

Another advantage of our methodology is that there is no need to construct basis sets with localized orbitals. Rather, self-consistent field calculations can be employed. Here we use density functional theory calculations at the B3LYP/6-31+G* level of theory.[8]

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[7] This was found to be the case for vinyl alcohol (Holt, J.; Karty, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 2797.)

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TABLE 1. Calculated[a] and Experimental Reaction Enthalpies

	propane						propene (parallel)						propene (perp)			
	acidity (kcal/mol)			HAE (kcal/mol)			acidity (kcal/mol)			HAE (kcal/mol)			acidity (kcal/mol)		HAE (kcal/mol)	
n	AM1	DFT	expt	AM1	DFT	expt	AM1	DFT	expt	AM1	DFT	expt	AM1	DFT	AM1	DFT
0	366.2	414.3[b]	415.6	317.6	309.0	307.1	335.9	387.6[c]	390.0	305.2	293.8	291.4	–	–	–	–
1	332.1	388.3	–	293.6	275.4	–	317.2	370.9	369.2	288.4	269.4	–	328.7	382.2	296.7	281.0
2	315.6	372.5	–	281.4	258.0	–	306.4	360.2	364.8	278.7	255.2	–	313.2	368.6	283.6	262.7
3	305.7	361.9	–	274.0	247.0	–	299.3	352.4	–	272.5	245.6	–	303.9	358.9	275.7	250.7

[a] DFT calculations were carried out at the B3LYP/6-31+G* level of theory. [b] Burk and Sillar (ref 12) obtained 414.4 kcal/mol using B3LYP/6-311+G**. [c] Merrill and Kass (ref 13) obtained 384.5 kcal/mol using BLYP/6-311++G(2df,2pd)//BLYP/6-31+G(d).

Additionally, we believe that hyperconjugation effects do not play a significant role in the acidity differences we examine. The effect of hyperconjugation between the σ framework of the CH_2 group and the π system of the C=C in the transition state of the allyl anion should be about the same as the hyperconjugation between the σ framework of the CH_3 group and the π system of the C=C in propene. In fact, Mo and Peyerimhoff[4] provide support for this assertion, calculating both of those interactions to be about 5 kcal/mol. Furthermore, we believe that the effect of hyperconjugation between the unhybridized p-orbital and the σ framework in the transition state of the allyl anion should be about the same as that of the analogous interaction in $CH_3CH_2CH_2^-$. Consequently, the extrapolation of the acidity difference between **7** and **6** back to $n = 0$ should well approximate the inductive effect of the vinyl group on the acidity of propene.

The extrapolation of the acidity difference between **5** and **6** to $n = 0$, on the other hand, will include a term resulting from the hyperconjugation in $CH_3CH_2CH_2^-$. However, the gas-phase acidities of methane, ethane, and propane (both primary and secondary protons) are all within about 4 kcal/mol of one another,[9] suggesting that this hyperconjugation term is not the major effect that dictates the enhanced acidity of propene over propane. Burk and Sillar further suggest that these acidity differences are determined largely "by the substituent electronegativity (field/inductive) and polarizability effects".[10]

We apply a parallel methodology in determining the resonance and inductive effects toward the enhanced hydride abstraction enthalpies (HAE's) of propene over propane.

Computational Methods

PC Spartan Pro (Wavefunction, Inc.) was employed to construct each molecular species and to perform geometry optimizations at the AM1 level of theory. Gaussian 98W was used to optimize the geometries with density functional theory (DFT) at the B3LYP/6-31+G* level,[8] using the AM1-optimized geometries as input geometries. Frequency calculations were performed on the DFT-optimized geometries in order to ensure that the stationary points were true minima, as well as to apply thermal corrections to the enthalpies.

Acidities were computed by subtracting the sum of the thermally corrected enthalpies of the proton and anion from that of the closed-shell neutral molecule. HAE's were computed by subtracting the sum of the thermally corrected enthalpies of the cation and hydride ion from the thermally corrected enthalpy of the closed-shell neutral molecule.

TABLE 2. Calculated[a] Differences in Reaction Enthalpy

	acidity enhancement (kcal/mol)				HAE enhancement (kcal/mol)			
	resonance[b]		inductive[c]		resonance[d]		inductive[e]	
n	DFT	AM1	DFT	AM1	DFT	AM1	DFT	AM1
1	11.3	11.5	6.1	3.6	11.6	8.3	−5.6	−3.1
2	8.4	6.9	3.9	2.4	7.5	4.9	−4.7	−2.2
3	6.5	4.5	3.0	1.8	5.1	3.2	−3.7	−1.7

[a] DFT calculations were carried out at the B3LYP/6-31+G* level of theory. [b] $\Delta_{acid}H°(\mathbf{7}) - \Delta_{acid}H°(\mathbf{5})$. [c] $\Delta_{acid}H°(\mathbf{6}) - \Delta_{acid}H°(\mathbf{7})$. [d] $\Delta_{HA}H°(\mathbf{7}) - \Delta_{HA}H°(\mathbf{5})$. [e] $\Delta_{HA}H°(\mathbf{6}) - \Delta_{HA}H°(\mathbf{7})$.

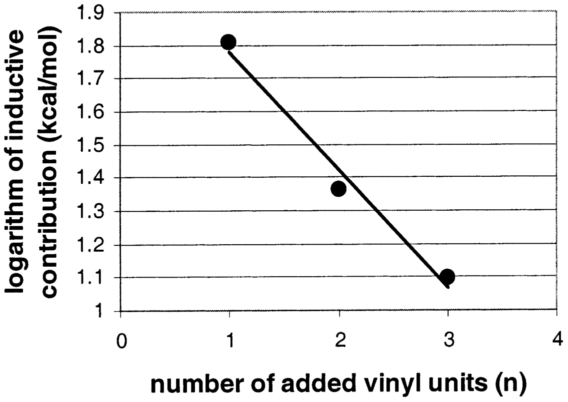

FIGURE 1. Inductive contribution by the terminal vinyl group toward the acidities of the $n = 1-3$ vinylogues of propene.

The added vinyl units in the vinylogues (**5**, **6** and **7**) were all in the (*E*) conformation. Therefore, the effects of (*E*)/(*Z*)-conformation on the thermodynamic properties of each species should largely cancel when computing the acidity and HAE differences between the propene and propane vinylogues.

Results

The acidities and HAE's for propane, propene, and their vinylogues are shown in Table 1. Also included in Table 1 are the available experimental values. Table 2 lists the contribution by resonance and inductive effects toward the enthalpies of each reaction. Figures 1−4 are plots of contributions by resonance and inductive effects toward the thermodynamics of each reaction involving the vinylogues, as a function of *n*.

Discussion

Derivation of Resonance Energies and Inductive Effects. The acidities and hydride abstraction enthalpies

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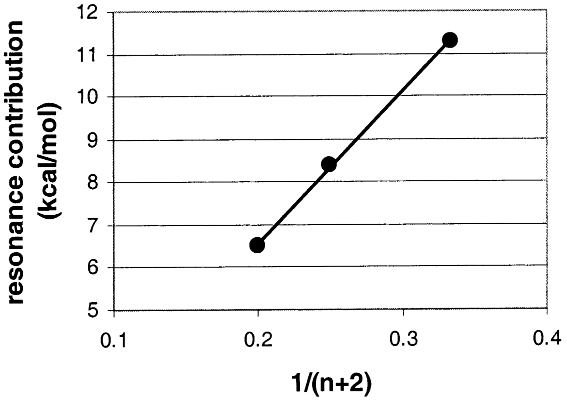

FIGURE 2. Resonance contribution by the terminal vinyl group toward the acidities of the $n = 1-3$ vinylogues of propene.

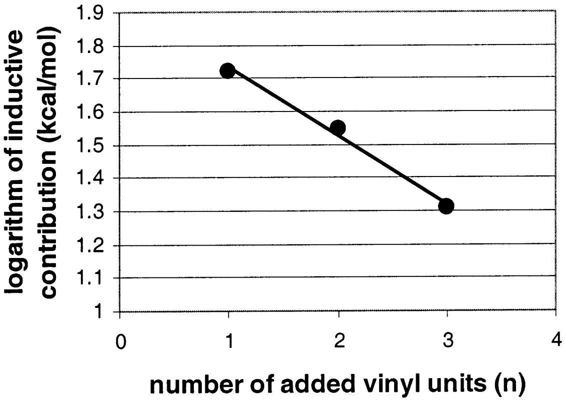

FIGURE 3. Inductive contribution by the terminal vinyl group toward the hydride abstraction enthalpies of the $n = 1-3$ vinylogues of propene.

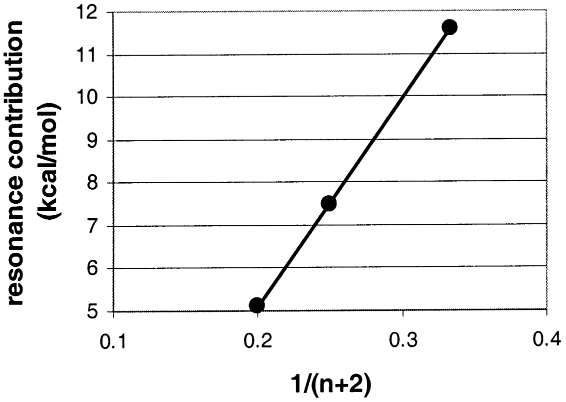

FIGURE 4. Resonance contribution by the terminal vinyl group toward the hydride abstraction enthalpies of the $n = 1-3$ vinylogues of propene.

calculated at the DFT level are in very good agreement with available experimental values (Table 1) as well as previous DFT calculations.[10,11] The differences between experimental and DFT values are all less than 5 kcal/mol, and most are within about 3 kcal/mol. However, the absolute enthalpies are not central to this work; rather, it is the calculated *differences* in enthalpy for which we expect significant cancellation of errors. This is evidenced by the excellent agreement between the calculated and experimental values for the acidity difference between propane and propene (26.7 and 25.6 kcal/mol, respectively), as well as the difference in HAE between propane and propene (15.2 and 15.7 kcal/mol, respectively). Additionally, the reaction enthalpy differences from our DFT calculations are in very good agreement with those from our low-level AM1 calculations (Table 2), whereas there is poor agreement between the AM1 and experimental absolute reaction enthalpies (Table 1). Furthermore, we have no reason to believe that errors in DFT-calculated acidity (or hydride abstraction enthalpy) differences are dependent on n. In our previous paper, we demonstrated excellent agreement of calculated differences in acidity between the B3LYP/6-31+G* level of theory, and the higher G2 level, for both the $n = 0$ parent compounds and the $n = 1$ vinylogues. In fact, the experimental acidities of the $n = 1$ and 2 vinylogues of propene (i.e. 1,3-pentadiene and 1,3,5-heptatriene) are in very good agreement with our DFT calculated acidities.

For each reaction examined, the reaction enthalpy becomes less positive (more exothermic) with increasing n. This can be rationalized in at least two ways. First, with each added vinyl unit, there is an additional resonance structure of the corresponding product ion (Figure 5), thereby stabilizing that ion.[12–15] Second, the more massive the species, the greater its polarizability, leading to additional internal solvation of the charge.[16]

To determine the resonance energy in the allyl cation and anion, we extrapolate the resonance contribution by the terminal vinyl group in the vinylogues of these ions to $n = 0$. It is clear that this resonance contribution in the vinylogues of both ions increases with decreasing n (Table 2, Figures 2 and 4). It therefore appears that the resonance contribution in the parent ions is at least that found in their respective $n = 1$ vinylogues. For the allyl cation, the resonance energy appears to be at least 11.6 kcal/mol, and for the allyl anion, it is at least 11.3 kcal/mol.

In our extrapolation of the resonance contribution of the terminal vinyl group to $n = 0$, we crudely estimate that that resonance contribution is proportional to $1/(n + 2)$. The reason for this is that in a given vinylogue of an allyl ion, the number of resonance contributors is $n + 2$, and we make the assumption that all contributors are equally important. This is similar to our extrapolation of the resonance contribution of the terminal vinyl group in vinyl alcohol to $n = 0$,[6] where we took the resonance contribution to be proportional to $1/(n + 1)$. The fit that we obtain for the allyl cation has an R^2 value of 0.9998, and that for the anion has an R^2 value 0.9984. The extrapolated resonance contribution in the allyl anion is 17.2 ± 1.1 kcal/mol, suggesting that the remainder of the 26.7 kcal/mol calculated enhancement of the acidity of

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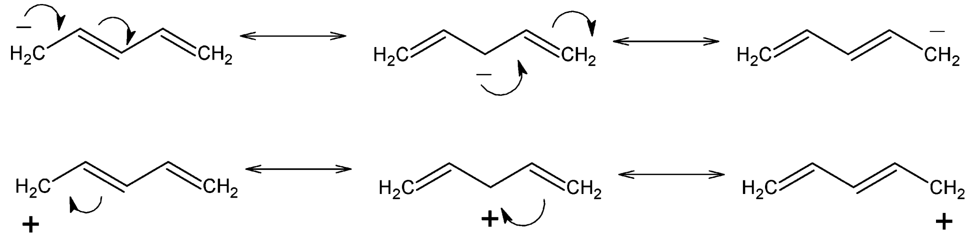

FIGURE 5. Resonance structures of the $n = 1$ vinylogues of the allyl anion (top) and the allyl cation (bottom). For each added vinyl unit, there is one additional resonance structure.

propene over ethane, i.e., 9.5 kcal/mol, is due to the inductive effects of the vinyl group. For the allyl cation, extrapolation of the vinyl group's resonance contribution to $n = 0$ yields 19.7 ± 0.5 kcal/mol. Since the difference in HAE between propene and ethane is calculated to be 15.3 kcal/mol, this suggests that the inductive contribution by the vinyl group toward the HAE is −4.4 kcal/mol. That is, the inductive effect of the vinyl group in propene serves to make hydride abstraction less favorable, by about 4 kcal/mol.

The inductive effects of the vinyl group toward the acidity and HAE enhancement of propene over propane can also be extrapolated directly. For the allyl anion, it appears that the inductive contribution increases monotonically with decreasing n (Table 2, Figures 1 and 3). Since the inductive contribution toward the acidity of the $n = 1$ vinylogue of propene is 6.1 kcal/mol, it can be said that the inductive contribution in the allyl anion itself is at least 6.1 kcal/mol. The function that we use to extrapolate the inductive effect is one that is exponential with n,[17] similar to our extrapolation of the inductive effect on the acidity of formic acid. Such an extrapolation ($R^2 = 0.9782$) yields 8.4 ± 1.0 kcal/mol, suggesting that about 8 kcal/mol of the acidity enhancement of propene over propane is due to inductive effects and that the remaining 18 kcal/mol acidity enhancement of propene over propane is due to resonance. Similarly, it appears that the inductive effect on the HAE of propene is more negative than −5.6 kcal/mol, the inductive effect on the HAE of the $n = 1$ vinylogue. Extrapolation using an exponential function ($R^2 = 0.9949$) yields −7.0 ± 0.2 kcal/mol as the inductive effect on the HAE of propene. Given that the HAE of propene is calculated to be more exothermic than that of propane by 15.3 kcal/mol, this suggests that the resonance energy of the allyl cation is about 22.3 kcal/mol. These values are in very good agreement with those obtained from the direct extrapolation of resonance in the vinylogues of the allyl anion to $n = 0$.

The fact that the inductive effect of the vinyl group on the acidity of propene is about equal in magnitude, but opposite in sign, to the inductive effect on the HAE of propene is consistent with a simple model. Namely, the vinyl group is taken to be effectively more electronegative than an ethyl group, as a result of the sp^2 hybridization instead of sp^3 hybridization.[13,14] The vinyl group is therefore expected to provide an electron-withdrawing effect on the neighboring CH_2^- in the allyl anion, resulting in extra stabilization of the charge. In the allyl cation, however, the same electron-withdrawing effect of the vinyl group is felt by the neighboring CH_2^+, thereby destabilizing the charge. We feel that the consistency of our results with such a simple model provides credibility to our methodology. Furthermore, the 8−10 kcal/mol contribution by inductive effects toward the acidity enhancement of propene over propane is consistent with the 9−11 kcal/mol contribution by inductive effects we obtained for the acidity enhancement of vinyl alcohol over methanol.[6]

Allyl Anion vs Formate Anion. The resonance energy of the allyl anion was calculated by Mo and coworkers[3,4] to be about 52 kcal/mol and about 47 kcal/mol, using an ab initio valence bond (VB) method and a block-localized wave function (BLW) method, respectively. Hiberty and Byrman calculated the resonance energy of the formate anion (HCO_2^-) to be about 40 kcal/mol,[18] using an ab initio valence bond method. It therefore appears that the resonance energy in the allyl anion is about 18%−30% greater than in the formate anion.

In our previous study,[6] we calculated the resonance contribution toward the acidity enhancement of formic acid (HCO_2H) over methanol (CH_3OH) to be about 13.5−15 kcal/mol, in agreement with several other authors.[5,18−20] These figures represent the difference between the resonance stabilization in the neutral formic acid molecule and that in the formate anion. This then suggests that the 13.5−15 kcal/mol is a lower bound for the resonance energy in the formate anion. Resonance theory, however, argues that the resonance stabilization in the neutral formic acid molecule should be a fraction of that in the formate anion. This is because a full negative charge is delocalized in the allyl anion, between two equivalent resonance structures; resonance in the neutral acid, on the other hand, serves to create a separation of charge. Consequently, the resonance energy of the formate anion should not be much greater than the 13.5−15 kcal/mol contribution toward the acidity enhancement. The resonance energy that we calculate for the allyl anion is about 17−18 kcal/mol, which is at most about 13%−30% greater than the resonance energy in the formate anion suggested by our previous study. It therefore appears that the relative resonance energies (fractional difference) of the allyl and formate anions calculated using our methodology are consistent with those calculated using the VB and BLW methods.

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To first approximation, one would expect the resonance energies of the allyl and formate anions to be about the same, given that both serve to delocalize a full negative charge between two identical atoms in a three-center π system. A better approximation of the relative resonance energies in the anions can be obtained using simple Hückel molecular orbital (HMO) theory.[21] The total HMO energy of the delocalized allyl anion is $4\alpha + 2.824\beta$. The energy of the localized system of a C=C double bond and a carbanion is $4\alpha + 2\beta$, suggesting that the resonance energy is 0.824β. For the delocalized formate anion, using empirically derived values[22] for the Coulomb integrals (H_{ii}) and the bond integrals (H_{ij}) involving oxygen atoms, the total HMO energy is $4\alpha + 7.577\beta$.[23] For the localized structure involving an isolated C=O and an oxyanion, the HMO energy is $4\alpha + 7\beta$, suggesting that the resonance energy is 0.577β. This suggests that the resonance energy of the allyl anion is about 43% greater than that in the formate anion, which is in good agreement with the results from our methodology, as well as from those using the VB and BLW methods.

Comparison of Methodologies. Wiberg's argument[2] that the resonance energy in the allyl anion is insignificant compared to that in the cation was supported primarily by examining rotational barriers of the CH_2 group in the cation versus the anion, and by making certain assumptions. Gobbi and Frenking[1] rejected such claims, suggesting that Wiberg's assumptions were unjustified and that his conclusions were based, in part, on a misunderstanding of the original definition of resonance energy. Gobbi and Frenking further showed, by examining the rotational barrier of the distorted anion, that the resonance energies of both the cation and the anion were about the same. It appears, however, that Gobbi and Frenking only provide qualitative arguments using their calculated rotational barriers and do not provide quantitative values for the resonance energies.

To our knowledge, Mo and co-workers[3,4] and Rablen[5] have been the only ones to provide quantitative values directly, without relying primarily on interpretations of the different rotational barriers in the cation and anion. Our results are in good quantitative agreement with the resonance energy of the allyl anion suggested by Raben's study (about 23 kcal/mol), but they are in significant quantitative disagreement with those provided by Mo and co-workers; our calculated resonance energies are about 25−30 kcal/mol smaller than those provided by Mo and co-workers. It therefore seems appropriate to examine more closely the results from our methodology and from theirs, which were obtained from calculations that impose restrictions on the wave functions of electrons within the ions.

It appears that the resonance energies calculated by Mo and co-workers (>45 kcal/mol) are overestimated. One reason is that their values are not consistent with the difference in acidity between propane and propene (eqs 1 and 3). Propene is more acidic than propane by 25.6 kcal/mol, which is taken to be primarily the sum of the resonance energy in the allyl anion and the inductive effects provided by the vinyl group. Therefore, 25.6 kcal/mol should roughly correspond to the upper bound for the resonance energy in the allyl anion. Mo and Peyerimhoff[4] call attention to hyperconjugation in propene that would raise this upper bound of 25.6 kcal/mol, but they also suggest, using results from their study, as well as from previous studies, that the hyperconjugation energy in propene is quite small, at around 3−5 kcal/mol. If inductive effects in the allyl anion are significant, as our results indeed suggest, this would lower the resonance energy in the allyl anion to a value substantially below 30 kcal/mol.

Further evidence that the methodology employed by Mo and co-workers overestimates resonance energies emerges when comparing their calculated resonance energy of the allyl radical to the homolytic bond dissociation energies (BDE's) of propane and propene. The BDE of propane (101.0 kcal/mol) is 12.9 kcal/mol greater than that of propene (88.1 kcal/mol). Because there are no atoms bearing formal charge in any species involved in the homolytic bond dissociation of propane or propene, inductive effects by the vinyl group are not expected to contribute significantly to that difference of 12.9 kcal/mol. It is therefore reasonable to assume that that difference is a relatively accurate reflection of the resonance energy in the allyl radical. If the 3−5 kcal/mol hyperconjugation energy of propene is taken into account, then the upper bound of the resonance energy of the allyl radical is 16−18 kcal/mol. However, Mo and co-workers calculate that resonance energy to be 28.4 kcal/mol.

We have applied our vinylogue methodology to derive the resonance energy of the allyl radical. To do so, the BDE's of **3**−**7** were calculated at the B3LYP/6-31+G* level of theory. Extrapolation of the resonance and inductive effects to $n = 0$ yielded 10.2 and 15.9 kcal/mol, respectively. These values are in good agreement with one another and are consistent with the upper bound for the resonance energy of the allyl radical derived above.

The specific reasons that might give rise to the overestimation of the resonance energies by Mo and co-workers are not clear. However, one possibility may be inherent in the ab initio VB calculations. Evidence of this comes from Hiberty and Byrman[18] (Mo and co-workers do not provide enough information to compare calculated reaction thermochemistries to experiment), who used ab initio VB calculations to calculate the acidities of formic acid (HCO_2H) to be 375.5 kcal/mol. The experimental acidity of formic acid is 345 kcal/mol,[9] which is different by 30 kcal/mol. In contrast, our moderate-level DFT calculations[6] were in disagreement by only 8 kcal/mol, and our G2 calculations were in disagreement by only 3.4 kcal/mol. Therefore, if ab initio VB calculations are in error by about 30 kcal/mol in calculating the acidity of formic acid (essentially the absolute difference in energy between two species), it should not be difficult to imagine an error of similar magnitude in calculating the resonance energy (also the absolute difference in energy between two species).

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[21] (a) Huckel, E. *Z. Phyzik* **1931**, *70*, 204. (b) Huckel, E. *Z. Phyzik* **1931**, *72*, 310. (c) Huckel, E. *Z. Phyzik* **1932**, *76*, 628. (d) Huckel, E. *Z. Phyzik* **1933**, *83*, 632.

[22] Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

[23] The empirical values used to obtain this result assumed distinct oxygen atoms—one that provided one electron to the system ($\alpha' = \alpha + \beta$; $\beta' = \beta$), and one that provided two electrons to the system ($\alpha' = \alpha + 2\beta$; $\beta' = 0.8\beta$). Assuming identical oxygen atoms, each being the average of the above two ($\alpha' = \alpha + 1.5\beta$; $\beta' = 0.9\beta$), the total HMO energy is nearly the same, at $4\alpha + 7.54\beta$.

One of the advantages that our methodology has is that it does not rely on absolute reaction thermochemistries. Rather, as mentioned earlier, it relies on *differences* in reaction thermochemistries, for which there is significant cancellation of errors that are introduced. We call attention once again to Tables 1 and 2, where it can be seen that the differences between our DFT-calculated and experimental *absolute* acidities are a few kcal/mol, yet the difference between DFT-calculated and experimental *relative* acidities are about 1 kcal/mol or less. This same cancellation of errors is much more dramatic with our AM1 calculations.

We reiterate that in the methodology we employ here, one of the key assumptions was that the hyperconjugation effects that appear in several species we examine largely cancel upon computing differences in acidity and HAE. If this assumption were the reason for the discrepancy between our results and those obtained by Mo and Peyerimhoff[4] and by Mo et al.,[3] then it follows that the hyperconjugation effects would have to be worth at least 20−30 kcal/mol. That is, the magnitude of the hyperconjugation effects in the allyl systems would have to meet, or exceed, the magnitude of the resonance energy that we estimate for the formate anion.

Allyl Cation vs Allyl Anion. It is interesting to note that the relative resonance energy we calculate for the allyl cation is slightly greater than that for the allyl anion—by about 2−5 kcal/mol. These results are in agreement with those of Mo et al.[3] One possible explanation was proposed by Wiberg et al.,[2] used to defend the notion that the allyl anion has very little resonance stabilization in comparison to the allyl cation. They point out that in the allyl cation, two electrons are delocalized over three centers, whereas in the ally anion, four electrons are delocalized. Additional electrostatic repulsion leads to a decreased stability. Whereas Gobbi and Frenking[1] suggest that such electron repulsion is not sufficient to lead to a drastic change in resonance stabilization, it may account for the few kcal/mol less resonance energy we observe in the allyl anion than in the cation.

The additional resonance energy in the allyl cation can also be justified in another way. The difference between the two species is essentially the number of electrons in the $1a_2$ orbital (i.e., the LUMO of the allyl cation and the HOMO of the allyl anion)—no electrons for the cation and two electrons for the anion. In the Hückel representation, this orbital is constructed from p orbitals out of phase with one another at the terminal carbons, with a node at the central carbon (Figure 6). Therefore, there is a through-space interaction between the p-orbitals of the terminal carbons that leads to destructive interference and, consequently, an antibonding type of interaction between the two carbon atoms.[24] Greater occupation of this MO should increase the extent of this interaction. Evidence of this phenomenon can be seen in the geometries of the allyl cation and anion, where it appears that the C−C−C bond angle is forced open to reduce the overlap between the terminal C atoms, and, consequently, the antibonding interaction. We calculate (B3LYP/6-31+G*) the C−C−C bond angle in the allyl cation to be 118.8° and that in the anion to be greater, at 132.1°.[25] In the resonance structures of each of these ions, where an isolated C=C double bond and an unhybridized p orbital do not interact, this antibonding interaction is presumably not present. Therefore, enabling resonance delocalization activates the antibonding interaction, creating additional angular strain in the anion than in the cation. This, in turn, should diminish the stabilization brought about by resonance in the anion, as compared to the cation.

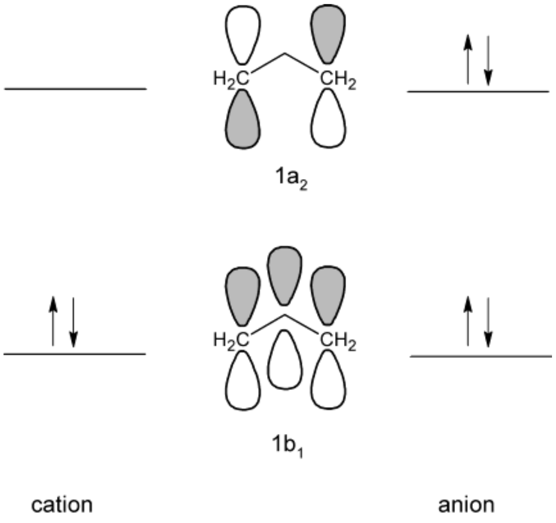

FIGURE 6. Hückel representation of the π orbitals of the allyl system. The occupancy of the $1a_2$ orbital introduces a through-space antibonding interaction between the ends of the system, forcing a more open C−C−C angle. The consequence is additional angular strain in the allyl anion.

Conclusions

Resonance energies of the allyl cation and anion were determined from calculated (B3LYP/6-31+G*) acidities and hydride abstraction enthalpies of **5**, **6**, and **7**, for $n = 1-3$. Our results suggest that the resonance energy of the allyl cation is 20−22 kcal/mol, whereas that of the allyl anion is 17−18 kcal/mol. These figures are in qualitative agreement with those calculated using localized wave functions, but are significantly smaller in magnitude.

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Supporting Information Available: Cartesian coordinates, energies, and number of imaginary frequencies of optimized geometries (B3LYP/6-31+G*) of all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] A similar antibonding interaction in enolate anions was used (Karty, J. M.; Janaway, G. J.; Brauman, J. I. *J. Am. Chem. Soc.* **2002**, *124*, 5213) to explain the dependence of cyclic ester enolate radical electron affinity on ring size.

[25] These angles are nearly identical to those obtained by Gobbi and Frenking (Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275) using MP2/6-31G(d) calculations.