Alkenes

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The Physical Origin of Saytzeff's Rule

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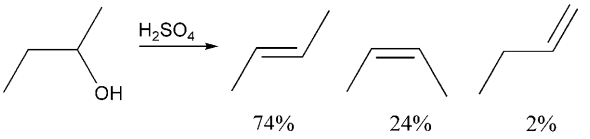
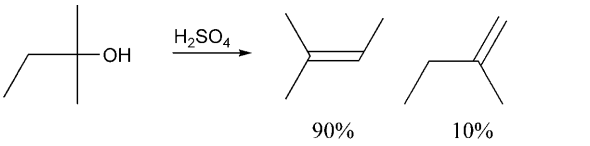
Alkene formation from elimination reactions is known to proceed by the preferential removal of the β hydrogen from the carbon atom that has the smallest number of hydrogen atoms. Initially formulated by A. Saytzeff to generalize the orientation in β-elimination reactions of alkyl halides,[1] this rule has been extended and generalized to other elimination reactions; for example, involving leaving groups other than halogens. The rule is valid for acid-catalyzed E1 reactions as well as base-induced E2 reactions, provided neither the base nor the β substituents are too bulky. Thus, in Equation (1), the



(1)

formation of both (*Z*)- and (*E*)-but-2-enes is preferred over that of but-1-ene upon the elimination of water.[2] Under similar experimental conditions, the branching ratio is smaller but still clear-cut as seen in Equation (2), which involves a tertiary alcohol.[3]



(2)

In an alternative formulation, the generalized Saytzeff rule states that elimination reactions occur by thermodynamic control, and that the most stable olefin is the one in which the double bond is more highly substituted. This empirical rule is widely taught in organic chemistry textbooks and leads to predictions that are generally confirmed by experimentally observed selectivities, as well as alkene stability measurements from heats of formation or heats of hydrogenation. However, the physical reason why the stability of olefins correlates with the degree of substitution around the double bond (as far as the substituents are of the alkyl type) has never been established, and different textbooks give different interpretations.

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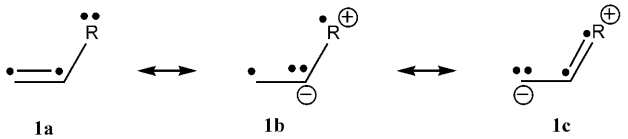
An interpretation in terms of hyperconjugation is often put forward.[4] In molecular orbital (MO) terms, hyperconjugation consists of the interaction between the highest occupied orbital of the alkyl fragment with the π* MO of the C=C bond. In valence bond terms, hyperconjugation is expressed as a resonance between several mesomeric structures, as exemplified in Scheme 1 wherein the electron pair of



Scheme 1. Hyperconjugation between a methyl group, R, and a double bond, as expressed in the VB language.

the pseudo-π orbital of a methyl fragment delocalizes over the two carbon atoms involved in the formal double bond. In this scheme, the stabilization associated to hyperconjugation is a result of the resonance energy arising from the mixing of the two minor structures, **1b** and **1c**, with the major structure **1a**. Of course, the question is how large is this stabilization energy.

Another explanation for the better stability of the more highly substituted alkene has been expressed in terms of hybridization of the C–C bonds.[5] Indeed, a $C(sp^2)$–$C(sp^3)$ bond is stronger than a $C(sp^3)$–$C(sp^3)$ bond, and the more substituents on the alkene the higher the ratio of $C(sp^2)$–$C(sp^3)$ bonds versus $C(sp^3)$–$C(sp^3)$ bonds. Notably, this explanation does not take into account the effect of hybridization on the C–H bonds, which supports anti-Saytzeff product formation (discussed below). Lastly, inductive effects and steric repulsions must also be considered.

Since hyperconjugation and hybridization effects are the most frequently invoked explanations, our strategy is to quantify them independently from each other, and this can be done by taking full advantage of the flexibility of ab initio valence bond (VB) methods,[6,7] which allow hyperconjugation to be turned "on" or "off".

The ab initio calculations will focus on the products of Equations (1) and (2), to understand the origin of their different relative stabilities. Figure 1 displays the geometries of these products, as optimized at the B3LYP density functional (DFT) level of theory. Among the two isomers of but-2-ene, only the most stable isomer, the *E*-isomer **2**, has been considered. In contrast, but-1-ene may adopt either a planar form (**3a**) having C_s symmetry, or a slightly more stable gauche form (**3b**). Similarly, the gauche form **5b** was experimentally found to be slightly more stable than the C_s form **5a** for the less substituted C_5H_{10} products of Equation (2). For technical reasons that will become clear below, hyperconjugation effects are more easily estimated for molecules having a C_s conformation compared to those

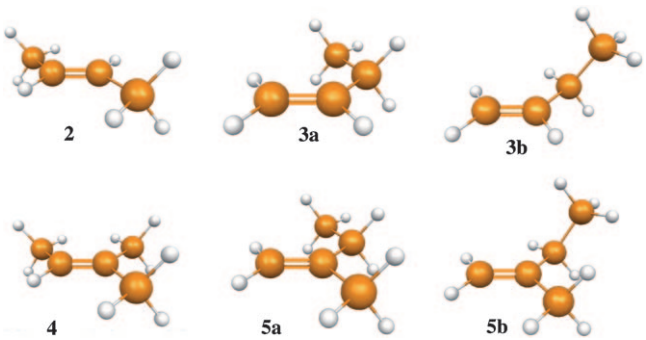


Figure 1. Conformations of but-2-ene (**2**), but-1-ene (**3a**, **3b**), methyl-but-2-ene (**4**), and 2-methyl-but-1-ene (**5a**, **5b**); **3a** and **5a** are C_s conformations, **3b** and **5b** are gauche conformations.

having a gauche conformation. Therefore, assuming that small hyperconjugation effects do not significantly vary with the rotation around the C–alkyl bond,[8] these will be estimated in the C_s forms and then carried over to the gauche forms.

The relative energies of species **2**–**5** are displayed in Table 1, as calculated at various levels of computation. The

Table 1: Experimental and calculated relative enthalpies and energies of alkene isomer.

Alkene	$\Delta\Delta H_f$ [kcal mol^{-1}] (Exp., 298 K)[a]	$\Delta\Delta H_f$ [kcal mol^{-1}] (G3, 298 K)	ΔE [kcal mol^{-1}] (G3, 0 K)	ΔE [kcal mol^{-1}] (RHF, 0 K)
but-2-ene (**2**)	0	0	0	0
but-1-ene (**3a**)[b]	–	2.73	2.51	3.15
but-1-ene (**3b**)[c]	2.43	2.59	2.42	2.60
methyl-but-2-ene (**4**)	0	0	0	0
2-methyl-but-1-ene (**5a**)[b]	–	1.09	0.96	0.95
2-methyl-but-1-ene (**5b**)[b]	1.53	1.36	1.20	1.07

[a] http//www.webbook.nist.gov/chemistry. The more substituted alkene is taken as zero-$\Delta\Delta H_f/\Delta E$ reference. [b] C_s conformation. [c] Gauche conformation.

enthalpies calculated at the G3 level at 298 K are in excellent agreement with the experimental enthalpies (compare ΔH_f values in Table 1). The energies (ΔE) calculated at 0 K and without zero-point energy corrections are also included. Interestingly, the ΔE values (G3, 0 K) are in very good agreement with those calculated using the simple restricted Hartree–Fock (RHF) level (RHF, 0 K). Although the ΔH_f value (G3) of the C_s form of C_5H_{10} (**5a**) is slightly lower than that of the gauche form (**5b**), we have confirmed that the gauche form is indeed the most stable at the level of G3 free energies, which takes entropy effects into account.

Let us now investigate in detail the reasons why the more substituted alkene isomers are more stable than the less substituted ones. When going from $CH_3CH{=}CRCH_3$ to $CH_2{=}$CREt, the following stabilizing/destabilizing effects are taking place:

i) loss of hyperconjugation, $\Delta E > 0$
ii) $C(sp^3){-}H \rightarrow C(sp^2){-}H$, $\Delta E < 0$
iii) $C(sp^2){-}CH_3 \rightarrow C(sp^3){-}CH_3$, $\Delta E > 0$
iv) π polarization in $CH_2{=}$CREt, $\Delta E < 0$
v) other effects (strain, σ-inductive effects, etc.)

As can be seen, a number of factors, destabilizing as well as stabilizing, have to be considered. Hyperconjugation will be considered first, and estimated by calculations allowing one to turn the delocalization "on" and "off" within the π system. In this spirit, several methods have been used in the past for the direct evaluation of the strength of conjugation and hyperconjugation, including natural bond orbital (NBO) analysis,[9] energy decomposition analysis (EDA),[10,11] and the block-localized wavefunction (BLW) method (a VB-type method),[12] which is the one used in the present work. A similar procedure has been applied for evaluating the energetic stabilization resulting from conjugation and hyperconjugation in various molecules,[8,12–15] as well as the π-aromatic energy in benzene and other systems.[16,17] The state with delocalization "on" will simply be the RHF wave function of the alkene, Ψ_{RHF}. The state with delocalization "off" will also be a wave function of the RHF type, but one in which the π-molecular orbitals are strictly localized either on the formal double bond, or on the substituents. This state, which is devoid of any hyperconjugation, will be referred to as Ψ_{BLW}. The hyperconjugation component of the energy, E_{HYPER}, will be estimated by Equation (3):

$$E_{HYPER} = E(\Psi_{BLW}) - E(\Psi_{RHF}) \qquad (3)$$

The E_{HYPER} quantities, as calculated for the isomers **2, 3a**, **4**, and **5a**, allow σ–π separation and are displayed in Table 2. First, consider the most substituted isomer of C_4H_8, but-2-ene (**2**). Orbital localization upon one of the two methyl groups raises the energy by 6.1 kcal mol^{-1}, whereas localizing both groups doubles the destabilization, which amounts to 12.2 kcal mol^{-1}.

Table 2: Estimations of the hyperconjugation effects (E_{HYPER}) for some substituted olefins.[a]

Localized groups	 2	 3a	 4	 5a
none	0	0	0	0
1-methyl	6.1	–	5.9–6.1[b]	5.9
2-methyl	12.2	–	12.2–12.3[b]	–
1-ethyl	–	6.4	–	6.4
all	12.2	6.4	18.4	12.3

[a] See Equation (3). All values reported in kcal mol^{-1}. [b] Depending on which methyl group(s) is (are) considered.

Similar values of destabilization are obtained for C_5H_{10} (**4** and **5a**) when one compares the localization over one methyl group (5.9–6.1 kcal mol^{-1}) or two methyl groups (12.2–12.3 kcal mol^{-1}); the values depend on which methyl groups are selected for the localization. Turning now to the hyperconjugative effect of the ethyl group in **3a** and **5a**, it is seen that localizing the sole ethyl group raises the energy by

6.4 kcal mol^{-1} in both molecules. From the previous results, assuming that each alkyl group brings a stabilization of approximately 6 kcal mol^{-1}, one expects hyperconjugation effects of approximately 18 kcal mol^{-1} for 2-methyl-but-2-ene (**4**) and 12 kcal mol^{-1} for 2-methyl-but-1-ene (**5a**), which is confirmed by the calculated values (see last row of Table 2). Therefore, for both C_4H_8 and C_5H_{10}, hyperconjugation effects stabilize the most substituted product by about 6 kcal mol^{-1}, which is significantly more than the actual thermodynamic preference expressed by Saytzeff's rule. It is therefore to be expected that the other effects support, all in all, the anti-Saytzeff product formation.

The effects of C–C and C–H hybridization changes (i) and ii) above) on the relative stabilities of **2**–**5** have been estimated from calculated or experimentally measured dissociation energies [Eqs. (4)–(7)]:

$$CH_3\text{-}CH{=}CH_2 \rightarrow {}^{\bullet}CH{=}CH_2 + CH_3{}^{\bullet} \quad (4)$$

$$2\,CH_3{}^{\bullet} \rightarrow C_2H_6 \quad (5)$$

$$H\text{-}CH_3 \rightarrow H^{\bullet} + CH_3{}^{\bullet} \quad (6)$$

$$H^{\bullet} + {}^{\bullet}CH{=}CH_2 \rightarrow C_2H_4 \quad (7)$$

In Equation (4), propene is stabilized relative to the dissociation products by a C(sp^3)–C(sp^2) bond, and by hyperconjugation between the methyl group and the π bond, the latter effect being estimated at 6 kcal mol^{-1} according to the calculations above. Therefore, the strength of the C(sp^3)–C(sp^2) bond, free of any other effect, can be estimated as the energy of the reaction in Equation (4), diminished by 6 kcal mol^{-1}. The energies of the remaining reactions [Eqs. (5)–(7)], quantify the strengths of a C(sp^3)–C(sp^3) bond, a C(sp^3)–H bond, and a C(sp^2)–H bond, respectively. The bond strengths are displayed in Table 3.

Table 3: Experimental and calculated (G3) bond strengths of some C–C and C–H bonds.

Entry	Eq.	Bond	Exp. values in kcal mol^{-1} (298 K)	G3 values in kcal mol^{-1} (0 K)
1	(4)	C(sp^3)–C(sp^2)	101.5 (95.5)[a]	106.6 (100.6)[a]
2	(5)	C(sp^3)–C(sp^3)	−89.8	−95.8
3	(6)	C(sp^3)–H	104.7	111.9
4	(7)	C(sp^2)–H	−111.1	−117.8

[a] Diminished by the hyperconjugation energy, 6.0 kcal mol^{-1}.

The experimental values at 298 K take zero-point energy corrections (ZPE) into account, whereas the G3 values do not and are consequently larger. Substituting a C(sp^3)–C(sp^2) bond for a C(sp^3)–C(sp^3) bond in a molecule raises the energy by 4.8 kcal mol^{-1} at 0 K (G3 level; Table 3, entries 1 and 2), all other things being equal. In contrast, substituting a C(sp^3)–H bond for a C(sp^2)–H bond now lowers the energy, by 5.9 kcal mol^{-1}, at the same computational level (Table 3, entries 3 and 4). As these two substitutions are involved when going from **2** to **3a** (or from **4** to **5a** as well), it follows that hybridization effects destabilize the more substituted alkene, relative to the less substituted one by 1.1 kcal mol^{-1}. Experimental measurements at 298 K (Table 3) yield a destabilization of the same order of magnitude, 0.7 kcal mol^{-1}. From these results, it appears that hybridization effects do not explain Saytzeff's rule, but on the contrary have an anti-Saytzeff effect that slightly reduces the effects of hyperconjugation.

Another effect that may possibly play a role in the relative stabilities of alkene isomers is the polarization of the π bond by the π-donating substituents. This π polarization has the effect of distorting the π-electron density of the double bond so as to diminish the repulsion between the π bond and the doubly occupied pseudo-π orbital of the alkyl group, and is therefore a stabilizing factor. Since there is some π polarization in **3a** but not in **2**, and expectedly more π polarization in **5a** than in **4**, this effect favors the less substituted alkenes, and therefore supports anti-Saytzeff product formation.

Like hyperconjugation, π polarization can be turned "on" and "off" at the level of VB calculations, more precisely in its generalized valence bond (GVB) form.[18] In this type of VB theory, the bond under study (here the π bond) is described as a singlet-coupled interaction between two orbitals, φ_1 and φ_2, which form a GVB pair. Thus, the ground state with π polarization "on" is represented by the wave function ψ_{GVB}^{on}:

$$\psi_{GVB}^{on} = |...\phi\bar{\phi}...(\varphi_1\bar{\varphi}_2 - \bar{\varphi}_1\varphi_2)| \quad (8)$$

Here φ_1 and φ_2 are the two quasi-atomic π orbitals involved in the π bond (see the Experimental Section for details), and φ is a generic term that represents all the remaining orbitals of the molecule. Since the π bond of the molecule is polarized, the orbitals φ_1 and φ_2 are different from each other. Therefore on can turn the polarization "off", by averaging φ_1 and φ_2 as in the wave function ψ_{GVB}^{off} below:

$$\psi_{GVB}^{off} = |...\phi\bar{\phi}...(\varphi_1^{av}\bar{\varphi}_2^{av} - \bar{\varphi}_1^{av}\varphi_2^{av})| \quad (9)$$

where φ_1^{av} and φ_2^{av} are constrained to be mirror images of each other. Moreover, to clearly separate π polarization from hyperconjugation both ψ_{GVB}^{on} and ψ_{GVB}^{off} are defined as devoid of any hyperconjugation, which is accomplished by localizing the π orbitals of all the alkyl groups in these wave functions. Accordingly, the stabilization energy resulting from π polarization, E_{POL}^{π}, is estimated by Equation (10):

$$E_{POL}^{\pi} = E(\psi_{GVB}^{off}) - E(\psi_{GVB}^{on}) \quad (10)$$

The results displayed in entry 3 of Table 4 show that π polarization is a weakly stabilizing factor, which amounts to 0.3, 0.58, and 0.16 kcal mol^{-1} in **3a**, **5a**, and **4**, respectively (the values for **3a** and **5a** are assumed to be transferable to **3b** and **5b** in Table 4). Therefore, all in all, this effect slightly favors the anti-Saytzeff products, as expected.

At this stage, the cumulated calculated effects of hyperconjugation, hybridization changes, and π polarization favor **2** over **3a** (or **3b**) by 4.45 kcal mol^{-1}, and **4** over **5a** (or **5b**) by 4.55 kcal mol^{-1}; these figures are larger than the actual stability energy differences, respectively 2.42 and 1.20 kcal mol^{-1}, as calculated at the G3 (0 K) level (Table 4, entry 5).

Table 4: Summary of the various effects that contribute to the thermodynamic difference between the Saytzeff products (**2** and **4**) and the anti-Saytzeff products (**3b** and **5b**).

Entry	Effect	**2**→**3b** (kcal mol^{-1})	**4**→**5b** (kcal mol^{-1})
1	Hyperconjugation	5.8	6.1
2	Hybridization changes	−1.1	−1.1
3	π polarization	−0.3	−0.4[a]
4	Other effects[b]	−2.0	−3.4
5	Total[c]	2.4	1.2

[a] Calculated as the difference between the stabilization effects of π polarization in **5a** (−0.58) and **4** (−0.16). [b] These include σ polarization and steric effects. [c] Calculated at the G3 (0 K) level.

These data mean that the remaining effects, which have not been considered up to now, support the anti-Saytzeff product formation.

These remaining effects can be thought of as being of two kinds. The first is σ polarization, by which the σ component of the double bond adapts itself to the alkyl σ-inductive effect, in the same way as the π component of the same bond adapts itself to the π-donating power of the alkyl substituent by π polarization. Thus, like this latter effect which has been investigated above, σ polarization is a stabilizing factor that is at work in but-1-ene but not in but-2-ene, owing to the symmetric disposition of the methyl groups in the latter. Alike, methyl-but-1-ene should be more stabilized by σ polarization than methyl-but-2-ene, which is less dissymetrically substituted. Thus, σ polarization is expected to favor the anti-Saytzeff product in both cases. Lastly, steric effects may also influence the relative stabilities of Saytzeff versus anti-Saytzeff products. As steric effects are not easy to separate from σ polarization by calculations, both effects are considered together (Table 4, entry 4) and found to amount to 2–3 kcal mol^{-1}, in support of the anti-Saytzeff product formation.

In summary, we have used ab initio valence bond theory to perform a direct estimation of hyperconjugative effects in some primary, secondary, and tertiary alkenes to trace the origin of the empirical Saytzeff rule. These effects have been found to be remarkably constant and additive, amounting to approximately 6 kcal mol^{-1} for each alkyl group. Accordingly, hyperconjugative effects favor the more substituted alkene by this same quantity, which is clearly more than necessary to account for the thermodynamic difference between the Saytzeff and anti-Saytzeff products. In contrast, hybridization effects, once separated from hyperconjugation, act in the opposite direction, as well as steric effects, inductive effects, and polarization of the double bond. Therefore, there emerges from the present study a clear picture of Saytzeff's rule as being entirely governed by hyperconjugation between the π bond and the π-donating substituents, whereas all other factors have an opposing effect.

Theoretical Section

The basic strategy of the block-localized wave function (BLW) method[12] is to partition the molecule or interacting system into subgroups, and to expand each localized molecular orbital in terms of primitive orbitals belonging to only one subgroup. The molecular orbitals belonging to the same subgroup are constrained to be mutually orthogonal, whereas those belonging to different subgroups are free to overlap. Within these constraints, the final block-localized wave function is optimized at the constrained Hartree–Fock level and is expressed by a Slater determinant. Here the subgroups that are subject to the localization/delocalization alternative are made of the π orbitals of the alkyl groups and the π orbital of the double bond, whereas the σ orbitals are delocalized in all cases. Owing to the non-orthogonality of the localized orbitals in the BLW wave function, this method is considered to belong to the VB family.

The generalized valence-bond method (GVB)[18] describes a two-electron bond as a formally covalent singlet coupling between two semi-localized orbitals. Let χ_a and χ_b be two purely localized atomic orbitals on centers A and B, respectively. The semi-localized orbitals φ_1 and φ_2 are defined as:

$$\varphi_1 = \chi_a + \varepsilon\chi_b \tag{11}$$

$$\varphi_2 = \chi_b + \varepsilon\chi_a \tag{12}$$

For a simple two-electron two-orbital case, the GVB wave function ψ_{GVB} is defined as:

$$\psi_{GVB} = |\varphi_1\bar{\varphi}_2 - \bar{\varphi}_1\varphi_2| \tag{13}$$

where the normalization is dropped, and the χ_a, χ_b orbitals and ε coefficients are optimized for self-consistency. The physical meaning of ψ_{GVB} is best visualized by expanding this wave function in terms of classical VB structures, constructed with purely localized orbitals:

$$|\varphi_1\bar{\varphi}_2 - \bar{\varphi}_1\varphi_2| = (1+\varepsilon^2)|\chi_a\bar{\chi}_b - \bar{\chi}_a\chi_b| + 2\varepsilon|\chi_a\bar{\chi}_a| + 2\varepsilon|\chi_b\bar{\chi}_b| \tag{14}$$

where the first term on the right-hand side of the equation is purely covalent, and the remaining ones are ionic. Therefore, despite its formally covalent aspect, the GVB wave function implicitly includes the optimized covalent versus ionic components of the A–B bond.

The XMVB program[19] has been used for the calculations of the BLW and GVB wave functions. The RHF and DFT calculations have used the Gaussian 03 package.[20] All calculations have been made with the standard cc-pVDZ basis set.

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