J. Phys. Chem. A **2005,** *109,* 9169−9173 **9169**

G3(MP2) Enthalpies of Hydrogenation, Isomerization, and Formation of Extended Linear Polyacetylenes

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Received: June 23, 2005

Motivated by our recent finding that, in contrast to their olefinic counterparts, linear alternant polyacetylenes (polyynes) show no appreciable thermodynamic evidence of conjugation stabilization, we have extended our G3(MP2) calculations of standard enthalpies of hydrogenation, $\Delta_{\rm hyd}H^\circ_{298}$, formation, $\Delta_{\rm f}H^\circ_{298}$, and isomerization, $\Delta_{\rm isom}H^\circ_{298}$, as far as isomeric dodecadiynes. We show that thermochemical stabilization of conjugated polyalkynes is about 1 kcal mol^{-1} over most of this range, and that the progression from one polyalkyne to the next is regular and additive. The longest chain polyalkynes, however, begin to revert to classical conjugation stabilization energies. For example, 5,7-dodecadiyne has a thermochemical stabilization enthalpy of 3.1 kcal mol^{-1}, approaching that of 1,3-butadiene. We also point out some of the difficulties encountered when one departs from Kistiakowsky's *operational* definition of conjugation stabilization. A cautionary example is drawn from the recent literature in which arguments of hyperconjugation and "virtual states" are used to arrive at, among other things, a value of 8.5 kcal mol^{-1} of conjugative stabilization in 1,3-butadiene.

I. Introduction

We recently found[1] that G3(MP2) computed values of the standard enthalpies of hydrogenation $\Delta_{\rm hyd}H^\circ_{298}$ of 1,3-butadiyne show no thermodynamically measurable conjugation stabilization comparable to the well-known stabilization of 1,3-butadiene. The method of measuring stabilization is straightforward and has been known for almost 80 years.[2] One simply compares $\Delta_{\rm hyd}H^\circ_{298}$ of the first double (or triple) bond with $\Delta_{\rm hyd}H^\circ_{298}$ of the second double (or triple) bond. In the case of 1,3-butadiene, this yields the familiar difference of 3.7 kcal mol^{-1} ascribed to conjugation stabilization, but in the case of 1,3-butadiyne, the difference is zero.

Some interest has been expressed in these calculations[3] so we continued the work, as described here, to examine the conjugation enthalpies of linear polyynes with three, four, and five alternant triple bonds, that is, we have examined molecules as large as 1,3,5,7,9-decapentayne. We find no evidence of significant stabilization of these more extended polyalkynes as judged by computed enthalpies of hydrogenation and isomerization. In contrast to the polyalkynes up to C_{10}, interior diynes begin to show a reversion to modest classical conjugation stabilization enthalpies. A case in point is 5,7-dodecadiyne, which is 3.1 kcal mol^{-1} more stable than 3,9-dodecadiyne.

The calculations show a very favorable agreement between G3(MP2) computed enthalpies of hydrogenation and experimental values in the literature. The progression in $\Delta_{\rm hyd}H^\circ_{298}$ from one alkyne to the next is additive and regular, which enabled us to develop a simple scheme for estimating $\Delta_{\rm hyd}H^\circ_{298}$ of linear polyalkynes as derivatives of acetylene using only $\Delta_{\rm hyd}H^\circ_{298}$(acetylene) and three additive enthalpic constants.

We discuss some of the logical pitfalls encountered when one strays from Kistiakowsky's simple *operational* definition of conjugation stabilization into realms of "hyperconjugation energies" and "virtual states". We show an example in which an excursion of this kind arrives at the unlikely conjugation stabilization of 8.5 kcal mol^{-1} for 1,3-butadiene and which draws from a collection of 15 adjustable parameters to explain the thermochemistry of 11 compounds, thereby achieving results that "agree superbly" with experiment.

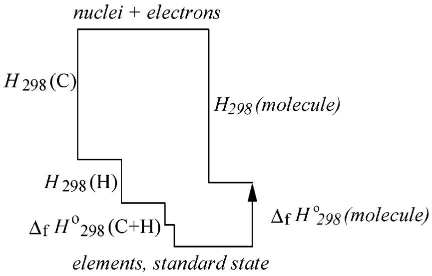

Figure 1. Thermochemical cycle for determination of $\Delta_{\rm f}H^\circ_{298}$ of a gas phase hydrocarbon.

II. Method

As in previous publications,[4] we calculate the G3(MP2)[5,6] enthalpy of formation of an alkyne in the standard state $\Delta_{\rm f}H^\circ_{298}$ from its total enthalpy of formation H°_{298} from isolated nuclei and electrons. We subtract $\Delta_{\rm f}H^\circ_{298}$(alkyne) from that of the corresponding alkane calculated in the same way to obtain the enthalpy of hydrogenation $\Delta_{\rm hyd}H^\circ_{298}$, also in the standard state. It should be noted here that computational thermochemistry is favored over experimental thermochemistry for larger alkynes which tend to polymerize or detonate.[7]

Figure 1 shows a thermochemical cycle for determination of $\Delta_{\rm f}H^\circ_{298}$ of a hydrocarbon. The top horizontal line represents the thermodynamic state of nuclei and electrons, the bottom horizontal line represents elements in their standard states, and the verticals, of which there are six, represent enthalpy changes. The three total enthalpy changes H_{298} represent falls from the

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10.1021/jp0534129 CCC: $30.25

TABLE 1: Enthalpies of Hydrogenation of Linear Alkynes (kcal mol^{-1}) at 298 K: Experimental, G3(MP2) Calculated,[6] Empirical, and Deviations d_1 and d_2

hydrocarbon	$\Delta_{hyd}H^\circ_{298}$(exp)	$\Delta_{hyd}H^\circ_{298}$(calc)	d_1[e]	$\Delta_{hyd}H^\circ_{298}$(emp)	d_2[f]
ethyne	−74.2 ± 0.2[a]	−74.3	0.1	−74.2	0.1
propyne	−69.3 ± 0.2[a]	−69.0	−0.3	−69.7	−0.7
1-butyne	−69.6 ± 0.3[a]	−69.6	0.0	−69.7	−0.1
2-butyne	−64.7 ± 0.3[a]	−65.0	0.3	−65.2	−0.2
1,3-butadiyne	−141.0 ± 2.0[a]	−139.1	−1.9	−138.5	0.6
1-pentyne	−69.6 ± 0.5[a]	−69.4	−0.2	−69.7	−0.3
2-pentyne	−65.9 ± 0.5[a]	−65.5	−0.4	−65.2	0.3
1,3-pentadiyne		−133.5		−134.0	−0.5
1,4-pentadiyne		−143.0		−143.0	−0.0
1-hexyne	−69.2 ± 0.1[b]	−69.4	0.2	−69.7	−0.3
2-hexyne	−65.7 ± 0.4[b]	−65.3	−0.4	−65.2	0.1
3-hexyne	−65.1 ± 0.3[b]	−66.0	0.9	−65.2	0.8
1,3-hexadiyne		−133.9		−134.0	−0.1
1,4-hexadiyne		−138.4		−138.5	−0.1
1,5-hexadiyne	−139.4 ± 1.0[c]	−139.6	0.2	−139.4	0.2
2,4-hexadiyne	−130.2[d]	−128.3	−1.9	−129.5	−1.2
1,3,5-hexatriyne		−203.7		−202.8	0.9
1-heptyne	−69.7 ± 0.4[b]	−69.4	−0.3	−69.7	−0.3
2-heptyne	−65.1 ± 0.3[b]	−65.3	0.2	−65.2	0.1
3-heptyne	−64.6 ± 0.4[b]	−65.8	1.2	−65.2	0.6
1,3-heptadiyne		−133.7		−134.0	−0.3
1,4-heptadiyne		−138.8		−138.5	0.3
1,5-heptadiyne		−135.2		−134.9	0.3
1,6-heptadiyne		−139.4		−139.4	0.0
2,4-heptadiyne		−128.7		−129.5	−0.8
2,5-heptadiyne		−134.0		−134.0	0.0
1,3,5-heptatriyne		−197.7		−198.3	−0.6
1,3,6-heptatriyne		−207.8		−207.3	0.5
1-octyne	−69.2 ± 0.6[b]	−69.4	0.2	−69.7	−0.3
2-octyne	−65.1 ± 0.1[b]	−65.4	0.3	−65.2	0.2
3-octyne	−64.8 ± 0.2[b]	−65.8	1.0	−65.2	0.6
4-octyne	−64.2 ± 0.3[b]	−65.6	1.4	−65.2	0.4
1,7-octadiyne	−139.7 ± 1.2[c]	−139.1	−0.6	−139.4	−0.3
1,3,5-octatriyne		−198.0		−198.3	−0.3
1,3,5,7-octatetrayne		−268.0		−267.1	0.9
1-nonyne	−69.5 ± 0.5[b]	−69.4	−0.1	−69.7	−0.3
2-nonyne	−65.1 ± 0.5[b]	−65.3	0.2	−65.2	0.1
3-nonyne	−64.7 ± 0.3[b]	−65.8	1.1	−65.2	0.6
4-nonyne	−64.7 ± 0.4[b]	−65.6	0.9	−65.2	0.4
1,3,5,7-nonatetrayne		−262.1		−262.6	−0.5
1,3,6,8-nonatetrayne		−272.7		−271.6	1.1
1-decyne	−69.6 ± 0.5[b]	−69.4	−0.2	−69.7	−0.3
2-decyne	−65.3 ± 0.5[b]	−65.4	0.1	−65.2	0.2
3-decyne	−64.9 ± 0.5[b]	−65.8	0.9	−65.2	0.6
4-decyne	−64.4 ± 0.4[b]	−65.6	1.2	−65.2	0.4
5-decyne	−64.1 ± 0.5[b]	−65.6	1.5	−65.2	0.4
1,3,5,7-decatetrayne		−262.4		−262.6	−0.2
1,3,5,7,9-decapentayne		−332.5		−331.4	1.1
1-dodecyne	−69.5 ± 0.5[c]	−69.4	0.1	−69.7	−0.3
2-dodecyne		−65.3		−65.2	0.1

[a] Reference 9. [b] Reference 8. [c] Reference 7d. [d] Reference 7a. [e] d_1 = exp − calc. [f] d_2 = emp − calc.

top state to the state of carbon atoms H°_{298}(C), hydrogen atoms H°_{298}, and the molecule in question H°_{298}(molecule) all in the gaseous state. The three verticals at the lower left represent enthalpies of formation $\Delta_f H^\circ_{298}$ of C and H from the standard state up to the gaseous state (two steps) and $\Delta_f H^\circ_{298}$(molecule) for the hydrocarbon in question, also in the gaseous state. For the sum of steps about the cycle to be zero, $\Delta_f H^\circ_{298}$(molecule) must be equal and opposite in magnitude to the remaining five steps

$$\Delta_f H^\circ_{298}(\text{molecule}) = -[H^\circ_{298}(\text{C}) + H^\circ_{298}(\text{H}) - \Delta_f H^\circ_{298}(\text{C}) - \Delta_f H^\circ_{298}(\text{H}) - H^\circ_{298}(\text{molecule})]$$

where the C and H enthalpies are multiplied by coefficients appropriate to the number of times they appear in the molecule. The standard enthalpy of hydrogenation is the difference between $\Delta_f H^\circ_{298}$(alkane) and $\Delta_f H^\circ_{298}$(alkene) or $\Delta_f H^\circ_{298}$(alkyne) because $\Delta_f H^\circ_{298}(H_2) = 0$ by definition.

III. Results

The computed G3(MP2) standard enthalpies of hydrogenation of acetylenes and polyacetylenes are given in Table 1 along with the experimental values where they are known. See also Supporting Information (Supporting Information 1, Table 1). Though in some cases experimental values were obtained under conditions that differ from the standard state, when a complete analysis has been carried out, deviations have been smaller than experimental uncertainty, therefore we ignore them. The mean absolute deviation between experimental values and G3(MP2)[6] calculated values is 0.64 kcal mol^{-1} but it includes differences between experimental values and standard state values, questionable experimental values for 1,3-butadiyne and 2,4-hexadiyne (no experimental uncertainty given), and errors due to the conformational mix of product alkane upon hydrogenation of interior alkynes, for example, 5-decyne.[8] Taking these factors into account, the overall reliability of the G3(MP2) calculations is probably about 0.4 kcal mol^{-1}. The signed mean deviation is 0.18 kcal mol^{-1}, indicating no bias toward positive or negative deviations. Having $\Delta_{\rm hyd}H^\circ_{298}$(alkyne), one can easily calculate its $\Delta_{\rm f}H^\circ_{298}$ from the experimental[9] or computed values (Supporting Information: SI 2, Table 2) of the corresponding $\Delta_{\rm f}H^\circ_{298}$(alkane).

There are remarkably simple and regular patterns in the values of $\Delta_{\rm hyd}H^\circ_{298}$ of the linear alkynes in Table 1.

(a) Substitution of an alkyl or ethynyl group on the triple bond of acetylene decreases $\Delta_{\rm hyd}H^\circ_{298}$ of that bond by 4.5 kcal mol^{-1}. Substitution of two groups decreases it by twice 4.5 kcal mol^{-1}.

(b) A conjugative arrangement of two triple bonds decreases $\Delta_{\rm hyd}H^\circ_{298}$ by 0.9 kcal mol^{-1}. Conjugation on both sides decreases it by twice 0.9 kcal mol^{-1}.

(c) When a sequence of $-$C≡C$-$CH$_2-$C≡C$-$ bonds exists, or in general a C(sp)$-$C(sp^3)$-$C(sp) linkage, the alkyne is *destabilized* by 3.6 kcal mol^{-1}, leading to a corresponding increase in $\Delta_{\rm hyd}H^\circ_{298}$. This value is revised from 3.9 kcal mol^{-1} reported previously.[10]

These patterns are used to calculate enthalpies of hydrogenation of linear alkynes and polyynes by treating all triple bonds as substituted acetylene, for which we take $\Delta_{\rm hyd}H^\circ_{298} = -74.2$ kcal mol^{-1}. An example of stepwise hydrogenation of 1,3,6-heptatriyne illustrates the method of calculating enthalpies of hydrogenation of various types of triple bonds.

$$\mathrm{HC{\equiv}C{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH} \rightarrow \mathrm{CH_3{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH}$$

One substituent and one conjugation: $-74.2 + 4.5 + 0.9 = -68.8$ kcal mol^{-1}.

$$\mathrm{CH_3{-}CH_2{-}C{\equiv}C{-}CH_2{-}C{\equiv}CH} \rightarrow \mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}CH}$$

Two substituents and elimination of the sp$-$sp$^3-$sp sequence: $-74.2 + 4.5 + 4.5 - 3.6 = -68.8$ kcal mol^{-1}.

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}CH} \rightarrow \mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

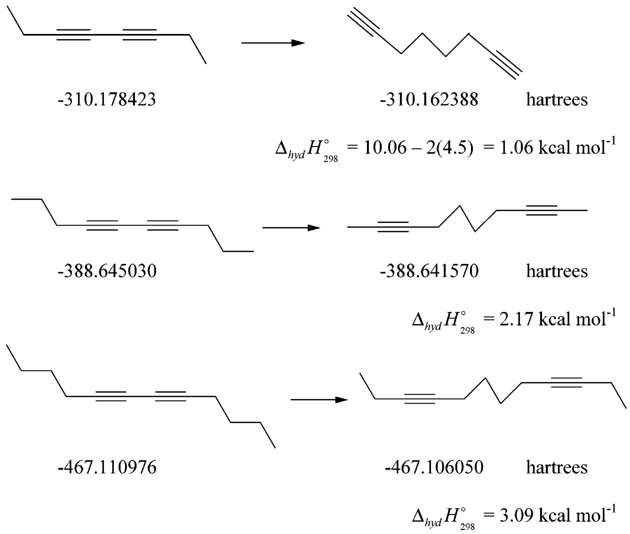
One substituent: $-74.2 + 4.5 = -69.7$ kcal mol^{-1}.

The total enthalpy of hydrogenation calculated empirically is -207.3 kcal mol^{-1}, compared to -207.8 kcal mol^{-1} by the G3(MP2) method. The order in which the bonds are considered hydrogenated does not, of course, affect the total value. For additional examples of the empirical calculation, see the Supporting Information (SI 3, Scheme 1).

Empirical enthalpies of hydrogenation so calculated are listed in Table 1 as $\Delta_{\rm hyd}H^\circ_{298}$(emp) and are in very good agreement with computed G3(MP2) values and with experimental values up to 1,3,5,7,9-decapentayne. The mean absolute deviation between $\Delta_{\rm hyd}H^\circ_{298}$(emp) and G3(MP2) values is 0.42 kcal mol^{-1} and the largest individual deviation is 1.2 kcal mol^{-1}. The signed mean deviation is 0.06, indicating no bias toward positive or negative deviation. The values calculated empirically show a mean absolute deviation of 0.45 kcal mol^{-1} from existing experimental values.

We were motivated to study 5,7-dodecadiyne and 3,9-dodecadiyne by the rather isolated thermochemical study of Flitcroft et al.[11] in which they found the former dialkyne to be 3.9 ± 0.9 kcal mol^{-1} more stable than the latter by comparison of the relevant enthalpies of hydrogenation. This constitutes a legitimate *thermodynamic* stabilization enthalpy and it should be equal to the difference in G3(MP2) total enthalpies of formation H°_{298}(molecule) in Figure 1. Comparison of H°_{298}(molecule) between isomers offers a direct way of arriving at thermochemical conclusions, circumventing uncertainties in enthalpies of formation of the elements in the standard state and High Level Corrections,[5] HLC, which cancel.

SCHEME 1: G3(MP2) Enthalpies of Isomerization[a]



[a] The enthalpies of isomerization are positive and are the difference in hartrees multiplied by 627.51 kcal mol^{-1} per hartree. The octadiyne isomerization was corrected by 2(4.5) to compensate for formation of two terminal triple bonds (see rule (a) above).

Typical stabilization (isomerization) enthalpies of about 1 kcal mol^{-1} for all the conjugated dialkynes in Table 1 to unconjugated isomers and of 3,5-octadiyne to 1,7-octadiyne in Scheme 1 are about 1 kcal mol^{-1}, consistent with the empirical estimation procedure. However, G3(MP2) values are 2.2 kcal mol^{-1} and rise to 3.1 kcal mol^{-1} for the decadiynes and dodecadiynes in Scheme 1. It is noteworthy that the calculated value of $\Delta_{\rm isom}H^\circ_{298}$ of 5,7-dodecadiyne to 3,9-dodecadiyne, 3.1 kcal mol^{-1}, is within the confidence limits of the value for the same isomerization, 3.9 ± 0.9 kcal mol^{-1}, found by comparing the corresponding heats of hydrogenation, measured experimentally by Flitcroft et al. a half-century ago.[11]

IV. Discussion

While confirming our computational results, Jarowski et al.[3] have made the argument that reckoning conjugation stabilization in this way is inappropriate for both conjugated diynes and dienes, in that it does not take into account stabilizations caused by the substitution of alkyl groups on double or triple bonds, often ascribed to “hyperconjugation”. Correcting for such stabilizations, they conclude that the “true” conjugation energy of diynes is 9.3 kcal mol^{-1}. They say, “The true conjugative stabilization is not a measurable quantity: it is the difference in energy between a conjugated molecule and its hypothetical energy (virtual state) if the entire contribution stemming from conjugation could be accounted for and excised.”[3] This definition of conjugative stabilization contrasts sharply with the currently accepted *operational* definition in terms of measurable quantities, to which we adhere. Constructing “virtual states” leads to logical contradictions best avoided, as we shall show.

It is a fact that substitution of alkyl groups stabilizes triple bonds, whether due to hyperconjugation or anything else.[12] Exothermicity of alkyne hydrogenation decreases by a fairly constant 4.5 kcal mol^{-1} per alkyl or alkynyl group substituted on the triple bond, as demonstrated by the accuracy of the $\Delta_{\mathrm{hyd}}H^{\circ}_{298}$(emp) values in Table 1 (Results, section (a)). In calculating stabilization energies due to substitution by one alkyl group, Jarowski et al. obtain 13 different values, depending on the choice of reference compound (their Supporting Information, Table 3), ranging from 6.1 kcal mol^{-1} of stabilization to −5.1 kcal mol^{-1} (destabilization), a span of 11.2 kcal mol^{-1}. In addition, two more conjugative stabilization values are available from their Supporting Information Table 4. This, in effect, provides 15 selectable parameters, to fit the 11 alkynes they treated.

For example, their Supporting Information Table 3 lists the hyperconjugative stabilization of 1,4-hexadiyne as −3.8 kcal mol^{-1} (destabilization), with propyne + 2-butyne as the reference compounds. Their Supporting Information Table 4, however, shows the hyperconjugative "correction" applied to the same compound to be 10.9 kcal mol^{-1}, with 2 × ethyne as the reference. With three alkyl groups substituted on the two triple bonds of 1,4-hexadiyne, the average hyperconjugative stabilization energy per alkyl group becomes $^{1}/_{3}(10.9) = 3.63$ kcal mol^{-1}, not −3.8 kcal mol^{-1}.

This internal inconsistency is further illustrated by the isomerization of eq 7 of Jarowski et al. (repeated below with their values of $\Delta_{\mathrm{hyd}}H^{\circ}_{298}$, in kcal mol^{-1}), where each single dash (−) indicates hyperconjugative stabilization by an alkyl group.

$$\underset{-133.7}{\mathrm{HC{\equiv}CC{\equiv}C{-}CH_2CH_3}} \rightarrow \underset{-137.7}{\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}C{-}CH_3}}$$

Using 5.7 kcal mol^{-1} of hyperconjugative stabilization for one alkyl group on one triple bond of the reactant but only 3.63 kcal mol^{-1} per alkyl group for the product resulted in the "true" conjugative stabilization of 9.2 kcal mol^{-1}, which they reported. However, if the same value of 5.7 were used for all postulated hyperconjugative stabilizations by an alkyl group in both reactant and product, the "true" conjugative stabilization similarly calculated would be 15.3 kcal mol^{-1}. If the value of 5.7 kcal mol^{-1} of hyperconjugative stabilization were retained for the reactant and the value of −3.8 kcal mol^{-1} for each alkyl substituent of the product from their Supporting Information Table 3 were used, then the "true" conjugative stabilization energy would be −13.2 kcal mol^{-1}, the negative sign indicating destabilization.

Jarowski et al.[3] contend that the enthalpy of hydrogenation of the first triple bond of 1,3-butadiyne should not be compared to that of the second triple bond, that of 1-butyne, because the triple bond of 1-butyne is stabilized by alkyl substitution, ascribed to hyperconjugation, while a triple bond in 1,3-butadiyne is not. They say that, in making judgments, the alkynes being compared must be balanced for hyperconjugation contributions. In the following comparison the number of hyperconjugation contributions (indicated by a dash) is balanced, two in each.

$$\mathrm{HC{\equiv}C{-}CH_2{-}C{\equiv}CH} \text{ vs } \mathrm{HC{\equiv}C{-}CH_2CH_2{-}C{\equiv}CH}$$

According to the Jarowsky treatment, there should be zero difference in the enthalpies of hydrogenation of the two compounds. In fact the G3(MP2) values are $\Delta_{\mathrm{hyd}}H^{\circ}_{298} =$ −143.0 and −139.6 kcal mol^{-1}, for the five-carbon vs the six-carbon compound ($\Delta_{\mathrm{hyd}}H^{\circ}_{298} = -142.9$ and −139.6 kcal mol^{-1} in Supporting Information Table 2 of Jarowski et al.). Similar results are obtained for four additional hyperconjugation-balanced comparisons: 1,4-heptadiyne vs 1,5-heptadiyne, with $\Delta_{\mathrm{hyd}}H^{\circ}_{298} = -138.8$ and −135.2 kcal mol^{-1}, respectively; 1,4-pentadiyne vs 1,6-heptadiyne, $\Delta_{\mathrm{hyd}}H^{\circ}_{298} = -143.0$ and −139.4 kcal mol^{-1}, respectively; 1,4-hexadiyne vs 1,5-heptadiyne, $\Delta_{\mathrm{hyd}}H^{\circ}_{298} = -138.4$ and −135.2 kcal mol^{-1}, respectively; and 1,4-pentadiyne vs 1,7-octadiyne, $\Delta_{\mathrm{hyd}}H^{\circ}_{298} = -143.0$ and −139.1 kcal mol^{-1}, respectively. In all of these cases the postulated hyperconjugation balance fails because one compound contains the bond sequence $\mathrm{{-}C{\equiv}C{-}CH_2{-}C{\equiv}C{-}}$ while the other does not. The unique instability introduced by this bond sequence was listed by Jarowski et al. in their Supporting Information Table 3 for both 1,4-pentadiyne and 1,4-hexadiyne, which are shown with negative stabilization energies (destabilization) due to hyperconjugation, but this was apparently disregarded subsequently in the difficult task of constructing "virtual states".

There may be merit to the proposal that stabilizations introduced by substituents on triple bonds be taken into account in trying to deduce a "true" conjugative stabilization. The difficulty with this approach is that it requires that a choice of reference compounds be made. This long-standing problem was discussed recently by Fishtik and Datta.[13] The argument of Jarowski et al.[3] is that conjugative stabilization should be calculated by reaction 1, where computed enthalpies of formation are shown below each compound and the resulting enthalpy of reaction $\Delta_{r}H^{\circ}_{298}$ is described as the "true" conjugation stabilization, for which a universal value of 9.3 ± 0.5 kcal mol^{-1} is proposed

$$\underset{2\times 54.3}{\mathrm{2HC{\equiv}CH}} + \underset{-30.2}{\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_3}} \rightarrow \underset{109.0}{\mathrm{HC{\equiv}C{-}C{\equiv}CH}} + \underset{2\times -20.1}{\mathrm{2CH_3{-}CH_3}} \quad (1)$$

resulting in $\Delta_{\mathrm{r}}H^{\circ}_{298} = -9.6$ kcal mol^{-1}.

Alternatively, one may choose different reference compounds and obtain similar or widely different values, as demonstrated by reactions 2−4. There are three types of bonds in all compounds in the set 1−4: C−H, C−C, and C≡C. These *isodesmic* reactions, in which the number and type of bonds is the same in reactants and products, would give the same result if this approach were valid. They do not.

Reaction 2 produces a somewhat lower value of conjugation stabilization than reaction 1.

$$\underset{2\times 39.4+(2\times 4.5)}{\mathrm{2HC{\equiv}C{-}CH_2{-}CH_3}} \rightarrow \underset{109.0}{\mathrm{HC{\equiv}C{-}C{\equiv}CH}} + \underset{-30.2}{\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_3}} \quad (2)$$

resulting in $\Delta_{\mathrm{r}}H^{\circ}_{298} = -9.0$ kcal mol^{-1}.

Reaction 3 produces a smaller enthalpy change

$$\underset{34.9+(2\times 4.5)}{\mathrm{CH_3{-}C{\equiv}C{-}CH_3}} + \underset{54.3}{\mathrm{HC{\equiv}CH}} \rightarrow \underset{98.3+(4.5)}{\mathrm{HC{\equiv}C{-}C{\equiv}C{-}CH_3}} + \underset{-17.8}{\mathrm{CH_4}} \quad (3)$$

resulting in $\Delta_{\mathrm{r}}H^{\circ}_{298} = -3.2$ kcal mol^{-1}.

Reaction 4 produces a much more exothermic value than the 9.3 kcal mol^{-1} proposed[3] for conjugation stabilization

$$\underset{2\times 54.3}{2HC{\equiv}CH} + \underset{-20.1}{CH_3{-}CH_3} \rightarrow \underset{109.0}{HC{\equiv}C{-}C{\equiv}CH} + \underset{2\times -17.8}{2CH_4} \qquad (4)$$

resulting in $\Delta_r H^\circ_{298} = -15.1$ kcal mol^{-1}.

Reactions 1−4 simply illustrate the well-known ambiguities that result from alternative and equally valid choices of reference compounds. Other simple examples are given in the Supporting Information (SI 4).

Prior to publication of our findings that there is no significant *thermochemically measurable* conjugative stabilization in simple diynes and polyynes, the intuitive anticipation would be that conjugative stabilization in alkynes should be approximately twice that of the commonly accepted value of about 3.7 kcal mol^{-1} for conjugated dienes, because 1,3-butadiyne has double the number of overlapping p orbitals relative to 1,3-butadiene. Jarowski et al.,[3] in fact, made exactly this argument and concluded that their conjugative stabilization in 1,3-butadiyne of 9.3 kcal mol^{-1} is entirely reasonable on the basis of 3.7 kcal mol^{-1} for conjugation in 1,3-butadiene. Their hyperconjugation arguments, however, also resulted in "true" conjugative stabilization of 8.2 in 1,3-butadiene, thereby sacrificing the very number they cite as a reasonable basis for their value for 1,3-butadiyne. In the end, they report that "true" conjugative stabilization enthalpies in dienes and diynes are about the same.

Once Kistiakowsky's path is abandoned, one is on a slippery slope. With a wide choice of reference compounds and hyperconjugative stabilizations available in the approach of Jarowski et al., there is ample flexibility to obtain "near perfect agreement" among the alkynes treated and to show that they "agree superbly" with the value of 9.3 ± 0.5 kcal mol^{-1} they reported for conjugative stabilization. For instance, one may speculate that the "true" conjugation stabilization in 1,3-butadiyne is 12.9 kcal mol^{-1}, but that this stabilization is almost completely counterbalanced by 12.0 kcal mol^{-1} of electron repulsion enthalpy among the 12 electrons H:C:::C:C:::C:H around the short C(sp)−C(sp) central bond. The result would be that only 0.9 kcal mol^{-1} of net stabilization would be detected experimentally. The sojourner on this logical path is then free to assign *any* value to the conjugation stabilization and then postulate counterbalancing electron repulsions just 0.9 kcal mol^{-1} smaller so as to match incontrovertible thermodynamic or computational fact.

In view of the vagaries involved in attempting to construct "virtual states" and the dependence on the choice of reference compounds, it appears that the *operational* definition of conjugation stabilization used by Kistiakowsky in terms of measured quantities or quantities that are measurable in principle is as valuable now as when it was first proposed[2] in that it provides an unambiguous way of reckoning stabilization of hydrocarbons with alternating double or triple bonds. The refusal to engage in speculation about physical phenomena that are not subject to experimental proof is not a weakness of the operational scientist, it is his hallmark. In this, the centennial of Einstein's *annus mirabilis*, we lesser scientists would be well advised to emulate his adherence to operational definitions, which remain steadfast in the shifting winds of qualitative theoretical fashion.

V. Conclusions

We have calculated G3(MP2) enthalpies of hydrogenation of linear alkynes up to 1,3,5,7,9-decapentyne and two dodecadiynes. We found good agreement with existing experimental values. A self-consistent pattern was found for the enthalpies of hydrogenation of linear alkynes, which allows a simple and accurate calculation of $\Delta_{hyd}H^\circ_{298}$, without recourse to selection of different reference compounds. Decadiynes and dodecadiynes exhibit a modest thermochemical conjugation stabilization. Shortcomings in a nonoperational interpretation of our results have been discussed.

Acknowledgment. We acknowledge grants of computer time from the National Science Foundation and the National Center for Supercomputing Applications.

Supporting Information Available: G3(MP2) energies and geometries of alkynes, calculated enthalpies of formation of linear alkanes, a scheme showing further examples supporting additivity relations given in the text, alternative isodesmic reactions extending eqs 1-4 in the text, and a complete Gaussian reference. This material is available free of charge via the Internet at http://pubs.acs.org.

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