instead of the distance of 2.97 Å found in the crystal structure. The present study points out that the energetics of the diad are sensitive to small changes in the relative orientation and the interatomic distances of the diad. It also points out the possibility that the proton shuttles between the two inner oxygens of the diad as the barrier for this shuttling is quite small when the inner oxygen distance is short. This may also contribute to the rigidity of the coplanar configuration of the diad. We find that the coplanar configuration of the diad is crucial for optimal binding of pepstatin. However, it has not been possible to keep the diad configuration coplanar during molecular mechanics and molecular dynamics calculations with the existing force field. We feel that the force field needs improvement for the special case of the Asp diad. One difficulty for parameterization of the interaction potential for this case is the limitation of the molecular mechanics approach to model the shuttling of the proton between the two oxygens. We are currently looking at different approaches to model this special part of the enzyme. We are also examining more closely the mobility of the Asp diad by more extensive molecular dynamics simulations of the enzymes with water or other substrates in the active site.

In the absence of improved force fields to mimic the configuration of the Asp diad, the use of constraints on the diad in our calculations gave results which are in good agreement with the experiments. Our results point out that the contribution of about 5 kcal/mol to binding from the hydroxyl group of the central statine residue is mainly due to the strong interaction of this group with the negatively charged Asp diad. It implies, therefore, that entropic contribution to the binding due to the displacement of the active site bound water molecule may not be significant. This raises the possibility that the water molecule is displaced even when pepstatin analogue lacking the hydroxyl group in *S* configuration binds to the enzyme. This may only be confirmed by further experimental studies. We feel that it is an important issue to be resolved because of its implications for designing strong inhibitors of aspartic proteinases and also for understanding their mechanism of action.

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**Registry No.** Asp, 56-84-8; pepsin, 9001-75-6; hydrogen ion, 12408-02-5; pepstatin, 26305-03-3; dehydroxypepstatin, 134486-20-7.

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# Ab Initio Calculations of the Relative Strengths of the $\pi$ Bonds in Acetylene and Ethylene and of Their Effect on the Relative Energies of $\pi$-Bond Addition Reactions

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**Abstract:** Energies at the CI-SD/6-31G** level have been calculated for acetylene, ethylene, ethane, and the vinyl and ethyl anions, radicals, and cations (classical and hydrogen-bridged). From these energies, the differences between the $\pi$-bond energies in acetylene and ethylene and between the energies of addition of $H^-$, $H^\bullet$, $H^+$, and $H_2$ to these $\pi$ bonds have been computed. Also reported are the calculated differences between the ionization potentials and between the electron affinities of the vinyl and ethyl radicals and between the energies required for formation of vinyl and ethyl anions, radicals, and cations from, respectively, ethylene and ethane. Excellent agreement is found between the calculated energies differences and those derived from the most recent experimental data. The differences between the energies of addition reactions to the $\pi$ bonds in acetylene and in ethylene are analyzed, and the effect of the nonlinear geometry of vinyl radical on the $\pi$-bond energy of acetylene is discussed.

The fact that the heat of hydrogenation of one $\pi$ bond in acetylene exceeds that of the $\pi$ bond in ethylene by 9 kcal/mol is commonly attributed to a weaker $\pi$ bond in the former molecule than in the latter.[1,2] As discussed in the Appendix, this explanation, in terms of a weaker $\pi$ bond in acetylene than in ethylene, appears to find support in comparison of the adiabatic C–C bond dissociation energies (BDEs) of acetylene, ethylene, and ethane. However, the C–C triple bond length (1.20 Å) is shorter than the C–C double bond length (1.34 Å), indicating that the p orbitals that form the $\pi$ bonds overlap better in alkynes than in alkenes. The better overlap between the p–$\pi$ orbitals in alkynes than in alkenes suggests[3] that each $\pi$ bond in acetylene is, in fact, *stronger* than the $\pi$ bond in ethylene.

As part of our explorations of the factors that affect the relative energies of $\pi$ bonds[4] and the ease of addition reactions to them,[4a,c,5] we have performed ab initio calculations in order to resolve this apparent paradox. We have computed the relative energies of the $\pi$ bonds in acetylene and ethylene and also the relative energies of the species formed by addition of a prototypical electrophile ($H^+$), radical ($H^\bullet$), and anion ($H^-$). The computational results reported here also provide information about the relative ease of formation of vinyl and ethyl cations, radicals, and anions from, respectively, ethylene and ethane.

## Computational Methodology

Ab initio calculations of absolute bond dissociation energies (BDEs) usually require large basis sets and inclusion of high levels

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(1) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; pp 288–98.

(2) McMurry, J. *Organic Chemistry*, 2nd ed.; Brooks/Cole: Pacific Grove, CA, 1984; pp 229–240.

(3) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; pp 11–16. Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*; Prentice-Hall: Englewood Cliffs, NJ, 1975; pp 9–11. Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982; p 19 and refernces therein. Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 8.

(4) (a) Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. (b) Hrovat, D. A.; Sun H.; Borden, W. T. THEOCHEM. **1988**, *163*, 51. (c) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710. (d) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (e) Coolidge, M.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1704. (f) Hammons, J. H.; Coolidge, M.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468. Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Phys. Org. Chem.* **1990**, *3*, 635.

(5) Getty, S. D.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4334.

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**Table I.** HF and CI-SD Energies (hartree) and HF Zero-Point Vibrational Energies (kcal/mol), Calculated with the 6-31G** Basis Set

| | HF[a] | CI-SD | ZPE |
|---|---|---|---|
| $C_2H_2$ | −76.821 837 3 | −77.076 638 2 | 18.4 |
| $C_2H_4$ | −78.038 841 4 | −78.321 539 5 | 34.2 |
| $C_2H_6$ | −79.238 235 0 | −79.549 688 5 | 49.7 |
| $C_2H_3^+$ | −77.084 433 1 | −77.338 470 7 | 22.9 |
| $C_2H_3^+$(clas) | −77.093 092 9 | −77.338 787 7 | 23.8 |
| $C_2H_5^+$ | −78.320 948 1 | −78.599 716 4 | 40.5 |
| $C_2H_5^+$(clas) | −78.320 597 0 | −78.593 195 0 | 40.1 |
| $C_2H_3^-$ | −77.338 346 8 | −77.615 670 8 | 23.7 |
| | −77.370 070 0[b] | −77.652 502 7[b] | 23.9[b] |
| $C_2H_5^-$ | −78.511 026 9 | −78.818 023 3 | 38.2 |
| | −78.540 101 4[b] | −78.854 143 5[b] | 38.3[b] |
| $C_2H_3^{\bullet}$ | −77.395 901 2 | −77.641 629 1 | 24.2 |
| | −77.400 001 8[b] | −77.647 756 4[b] | 24.2[b] |
| $C_2H_3^{\bullet}$ (linear) | −77.383 544 3 | −77.631 270 3 | 22.4 |
| $C_2H_5^{\bullet}$ | −78.605 525 4 | −78.887 238 7 | 39.5 |
| | −78.607 663 4[b] | −78.891 461 9[b] | 39.4[b] |

[a] RHF for closed-shell species and UHF for radicals. [b] With the 6-31++G** basis set.

of electron correlation.[6] Since we were not interested in calculating absolute BDEs, we were able to take advantage of the cancellation of errors that tends to occur when only the relative energies of two similar types of bonds are required.[7]

Geometries were optimized and vibrational analyses were performed with the 6-31G** basis set,[8] with use of RHF calculations for closed-shell species and UHF calculations for radicals.[9] For calculations on anions the basis set was augmented with a set of diffuse functions on all atoms (6-31++G**).[10] The total and zero-point energies that were obtained are listed in Table I.

Also given in Table I are the total energies calculated with the inclusion of electron correlation at the CI-SD level. For radicals, CI-SD calculations, which give pure doublet wavefunctions, are preferable to UMP calculations, which give correlated wavefunctions that are contaminated by higher spin states. All the calculations reported here were performed with the Gaussian 86 package of ab initio programs.[11]

## Results and Discussion

We begin by verifying that energies calculated at the CI-SD/6-31G** level would correctly reproduce the greater exothermicity of the hydrogenation of acetylene,

$$HC{\equiv}CH + H_2 \rightarrow H_2C{=}CH_2 \tag{1}$$

relative to the hydrogenation of ethylene

$$H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3 \tag{2}$$

The difference between the reactions in eqs 1 and 2 is the reaction

$$HC{\equiv}CH + H_3C{-}CH_3 \rightarrow 2H_2C{=}CH_2 \tag{3}$$

As shown in Table II, the energy change for this reaction at the CI-SD level, after correction for zero-point energy differences, is calculated to be −10.2 kcal/mol, which compares favorable with the experimental value of $\Delta\Delta H°_{H_2} = -9.4$ kcal/mol.[12] With this assurance that we could accurately calculate the energy difference whose origin we wanted to investigate, we turned to the calculation of the relative $\pi$-bond energies of the unsaturated molecules in eq 3.

**Table II.** Calculated CI-SD/6-31G** Energy Changes (kcal/mol) for the Reactions Indicated, and with Correction for Zero-Point Energies

| | $\Delta E$ | $\Delta E + \Delta$ZPE |
|---|---|---|
| $C_2H_2 + C_2H_6 \rightarrow 2C_2H_4$ | −10.5 | −10.2 |
| $2C_2H_5^{\bullet} + C_2H_2 \rightarrow 2C_2H_3^{\bullet} + C_2H_6$ | 11.4 | 12.0 |
| $C_2H_3^{\bullet} \rightarrow C_2H_3^{\bullet}$(linear) | 6.5 | 4.7 |
| $C_2H_5^{\bullet} + C_2H_4 \rightarrow C_2H_6 + C_2H_3^{\bullet}$ | 11.0 | 11.1 |
| $C_2H_5^{\bullet} + C_2H_2 \rightarrow C_2H_4 + C_2H_3^{\bullet}$ | 0.4 | 0.9 |
| $C_2H_5^{\bullet} + C_2H_3^- \rightarrow C_2H_3^{\bullet} + C_2H_5^-$ | 27.1 | 26.3 |
| | 26.4[a] | 25.6[a] |
| | 27.6[b] | 26.7[b] |
| $C_2H_5^- + C_2H_2 \rightarrow C_2H_4 + C_2H_3^-$ | −26.7 | −25.4 |
| | −27.1[b] | −25.8[b] |
| $C_2H_3^{\bullet} + C_2H_5^+ \rightarrow C_2H_5^{\bullet} + C_2H_3^+$ | 9.8 | 7.6 |
| | 5.5[c] | 4.5[c] |
| $C_2H_5^+ + C_2H_2 \rightarrow C_2H_4 + C_2H_3^+$ | 10.3 | 8.5 |
| | 6.0[c] | 5.4[c] |
| $C_2H_5^+$(classical) $\rightarrow C_2H_5^+$ | −4.1 | −3.7 |
| $C_2H_3^+$(classical) $\rightarrow C_2H_3^+$ | 0.2 | −0.6 |
| $C_2H_5^- + C_2H_4 \rightarrow C_2H_6 + C_2H_3^-$ | −16.2 | −15.2 |
| | −16.6[b] | −15.6[b] |
| $C_2H_5^+ + C_2H_4 \rightarrow C_2H_6 + C_2H_3^+$ | 20.8 | 18.7 |
| | 16.5[c] | 15.7[c] |

[a] 6-31++G** for both anions and radicals. [b] 6-31++G** for anions only. [c] For classical carbocations.

The $\pi$-bond energy of ethylene can be taken as either the activation energy required to interconvert *cis*- and *trans*-1,2-dideuterioethylene[13] or as the negative of the energy of the disproportionation reaction,[14]

$$2H_3C{-}CH_2^{\bullet} \rightarrow H_2C{=}CH_2 + H_3C{-}CH_3 \tag{4}$$

Using the heats of formation of ethylene and ethane[12] and the currently accepted value for the heat of formation of the ethyl radical,[15] eq 4 gives a $\pi$-bond energy of 64 kcal/mol for ethylene. This thermodynamic value is essentially the same as the value of 65 kcal/mol, obtained from the kinetics for cis–trans isomerization.[13] Calculations using the two different definitions also give very similar values, which, when electron correlation is included, are close to those obtained experimentally.[4d,16]

In the case of acetylene only the thermodynamic definition of the energy of one $\pi$ bond can be used. By analogy to eq 4, the relevant disproportionation reaction is

$$2H_2C{=}CH^{\bullet} \rightarrow HC{\equiv}CH + H_2C{=}CH_2 \tag{5}$$

This reaction may be viewed as measuring the energy lowering that occurs when two vinyl radical centers are placed on adjacent carbons, so that the second $\pi$ bond that is present in acetylene is formed.

Subtracting eq 5 from eq 4 yields

$$2H_3C{-}CH_2^{\bullet} + HC{\equiv}CH \rightarrow 2H_2C{=}CH^{\bullet} + H_3C{-}CH_3 \tag{6}$$

whose energy gives the difference in $\pi$-bond energies between acetylene and ethylene. As shown in Table II, the calculated energy change for the reaction in eq 6 is 12.0 kcal/mol, so that our calculations find a $\pi$ bond in acetylene to be stronger than the $\pi$ bond in ethylene by this amount.

Experimental data are available that support this calculated value for the difference in $\pi$-bond energies. From a heat of formation at 0 K of $\Delta H_f° = 72.7$ kcal/mol for the vinyl radical,[17,18]

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(6) See for example, Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(7) Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 271–324.

(8) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(9) Optimized geometries in Z matrix format are available as supplementary material. Ordering information is given on any masthead page.

(10) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R.; *J. Comput. Chem.* **1983**, *4*, 294. Pople, J. A.; Seeger, R.; Krishnan, R. *J. Chem. Phys.* **1984**, *80*, 3265.

(11) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, R.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Rohlfing, C. M.; Kahn, L. R. Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E.; Pople, J. A., Carnegie-Mellon University, 1986.

(12) Cox, J. P.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(13) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(14) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63–65.

(15) (a) Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57 and references cited therein. (b) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114.

(16) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057.

(17) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(18) This experimental value is in excellent agreement with the values indicated by two different sets of ab initio calculations: (a) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1988**, *88*, 7405. (b) Wu, C. J.; Carter, E. A. *J. Am. Chem. Soc.* **1990**, *112*, 5893.

an experimental value of 76 kcal/mol is obtained from eq 5 for the energy of a $\pi$ bond in acetylene. Thus, experimental heats of formation indicate that a $\pi$ bond in acetylene is 12 kcal/mol stronger than the $\pi$ bond in ethylene, in perfect agreement with our CI-SD/6-31G** value of 12.0 kcal/mol.

Previous work has shown that pyramidalization of radical centers weakens $\pi$ bonds to them by the amount of energy required to planarize these centers to their $\pi$-bonded equilibrium geometries.[4] Both UHF and CI-SD calculations find that planarization of ethyl radical requires less than 0.2 kcal/mol. Thus, pyramidalization of ethyl is computed to have a negligible effect on the $\pi$-bond energy of ethylene.

In contrast, the experimentally observed preference of vinyl radical for a bent geometry[19] has a significant effect on reducing the energy of a $\pi$ bond in acetylene. We find that linearizing the vinyl radical is computed at the CI-SD/6-31G** level to require 6.5 kcal/mol, which is reduced to 4.7 kcal/mol after correction for the difference in zero-point energies of the two geometries. These values are close to those computed previously by Paddon-Row and Pople.[20] They attributed the fact that the calculated barrier to linearization is about 2 kcal/mol higher than that found experimentally[19] to a contribution from tunneling to the measured rate.

The energy required to linearize the two vinyl radical centers in forming acetylene is calculated to weaken the $\pi$ bond formed by 9.5 kcal/mol. Put another way, if the energy of the disproportionation reaction in eq 5 were recalculated with two linear radical centers on the left-hand side of the equation, the computed $\pi$-bond energy of acetylene would increase by 9.5 kcal/mol and become fully 21.5 kcal/mol greater than the $\pi$-bond energy of ethylene.

As noted above, using the energy of the bent vinyl radical, we calculate that the energy of a $\pi$ bond in acetylene is 12.0 kcal/mol stronger than the $\pi$ bond in ethylene, a finding that is in excellent agreement with experimentally based estimates of the difference in $\pi$-bond energies. Clearly, a weaker $\pi$ bond in acetylene than in ethylene cannot be responsible for the difference in their heats of hydrogenation. The heat of hydrogenation of acetylene exceeds that of ethylene, *not because of*, *but in spite of* the difference in the strengths of their $\pi$ bonds.

Since the greater heat of hydrogenation of acetylene cannot be attributed to a weaker $\pi$ bond that is broken, the larger heat of hydrogenation of acetylene must be due to the greater strength of the C–H $\sigma$ bonds that are formed. This conclusion is verified by subtracting eq 6, which gives the difference in the $\pi$-bond energies, from eq 3, which gives the difference in hydrogenation energies. Equation 7 is obtained. This equation shows that the

$$2H_3C{-}CH_3 + 2H_2C{=}CH^\bullet \rightarrow 2H_2C{=}CH_2 + 2CH_3CH_2^\bullet \quad (7)$$

difference between the hydrogenation energies and the $\pi$ BDEs is just twice the difference between the BDEs of a C–H bond in ethane and a C–H bond in ethylene.

From the values already given for the CI-SD/6-31G** energies associated with eqs 3 and 6, an energy of −22.2 kcal/mol is obtained for eq 7. The calculated value of 11.1 kcal/mol for the difference between the BDE of a C–H bond in ethylene and in ethane is in excellent agreement with the difference of about 11 kcal/mol between the most recent experimental estimates of these two BDEs.[15,17]

It is interesting to note that a difference of about 11 kcal/mol between the strengths of C–H bonds at trigonal and tetrahedral carbons also accounts for the experimental fact that the heat of hydrogenation of allene to propene exceeds that of propene to propane by 10.7 kcal/mol.[12] In both hydrogenation reactions a double bond is broken. However, the two reactions differ by the fact that in the hydrogenation of allene to propene, a C–H bond is formed at a carbon that is trigonal in the product, whereas in the hydrogenation of propene to propane, both new C–H bonds are formed at carbons that are tetrahedral in the product.

The calculated difference of 11.1 kcal/mol between the C–H BDEs for trigonal and tetrahedral carbons is nearly the same as the calculated difference of 12.0 kcal/mol between $\pi$-bond energies in triple and double bonds. Since, in the addition of a hydrogen atom to the $\pi$ bonds of acetylene and ethylene, a $\pi$ bond is broken and a new C–H bond is made, the greater strength of the $\pi$ bond being broken in acetylene is almost exactly balanced by the greater strength of the C–H bond formed at the trigonal carbon in the vinyl radical. Consequently, the energy difference between the two hydrogen atom addition reactions, which is given by the energy of the reaction in eq 8, is calculated to be only 0.9 kcal/mol at the CI-SD/6-31G** level.

$$H_3C{-}CH_2^\bullet + HC{\equiv}CH \rightarrow H_2C{=}CH_2 + H_2C{=}CH^\bullet \quad (8)$$

Since eq 8 is just the difference between eq 3 and half of eq 7, and since our calculated values for the differences in hydrogenation energies[12] and C–H BDEs[15,17] are in good agreement with experiment, so is the calculated value of about 1 kcal/mol for eq 8. If this finding of a slightly greater exothermicity for addition of a hydrogen atom to ethylene than to acetylene were extrapolated to the *transition states* for addition of hydrogen and other free radicals to double and triple bonds, one might expect alkenes to be slightly more reactive than alkynes to free radical addition reactions. This does appear generally to be the case.[21,22]

If the unpaired electron on both sides of eq 8 is replaced by a negative charge, eq 9 for the energy difference between addition of hydride ion to ethylene and acetylene is obtained. The energy

$$H_3C{-}CH_2^- + HC{\equiv}CH \rightarrow H_2C{=}CH_2 + H_2C{=}CH^- \quad (9)$$

changes associated with these two equations differ only by the difference between the electron affinities of the ethyl and vinyl radicals. Our CI-SD calculations with the 6-31++G** basis set for the anions find that the vinyl radical has the greater electron affinity by 26.7 kcal/mol. The calculated *difference* in electron affinities does not appear to be very dependent on inclusion of diffuse functions, since the CI-SD value with the 6-31G** basis set for the anions as well as the radicals is 26.3 kcal/mol.

Recent measurements give a value of 15.5 kcal/mol for the electron affinity of vinyl radical.[17] As predicted computationally,[23] experimentally the ethyl anion appears to be unbound.[24,25] The electron affinity of ethyl radical has been estimated to be −6.4 kcal/mol,[24] which gives an experimental estimate of 22 kcal/mol for the difference between the electron affinities of the two radicals. This difference is about 5 kcal/mol less than that computed by us.

Because eq 8 is nearly themoneutral, eq 9 is computed to be exothermic by 25.8 kcal/mol, essentially the same amount by which the electron affinity of the nominally sp$^2$ orbital in vinyl radical is calculated to exceed that of the nominally sp$^3$ orbital in ethyl radical. This finding supports the commonly held belief that nucleophiles add more easily to alkynes than to alkenes[1] because of the larger amount of 2s character in the atomic orbital where the negative charge resides in the product.[22,26]

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(19) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(20) Paddon-Row, M. N.; Pople, J. A. *J. Phys. Chem.* **1985**, *89*, 2768.

(21) Nagase, S.; Kern, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 4513 and references therein.

(22) Reviews of acetylene chemistry: Viehe, H. G. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1979. *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978.

(23) Schleyer, P. von R.; Spitznagel, G. W.; Chandrasekhar, J. *Tetrahedron Lett.* **1986**, *27*, 4411.

(24) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968.

(25) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2506.

(26) Additions of nucleophiles to alkynes may also be favored kinetically over additions to alkenes by the lower energetic cost of trans bending of alkynes, compared to trans pyramidalization of alkenes. These deformations lower the LUMO energies in the transition states for these two addition reactions, and moreover, greater LUMO lowering is provided by alkyne bending than by a comparable amount of ethylene pyramidalization.[27] The same effect probably is also operative in the transition states for radical additions, but, as would be expected, calculations find it to be less important when the attacking species is a hydrogen atom,[21] rather than a hydride ion.

(27) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

However, this explanation is correct only because the greater strength of the $\pi$ bond that is broken in the alkyne is approximately cancelled by the greater strength of the C–H $\sigma$ bond in the vinyl radical. This near cancellation allows the relative amounts of stabilization provided for the additional electron, which is present in the anions formed by hydride addition but not in the radicals generated by addition of hydrogen atoms, to control the differences in energetics.

The difference between the protonation energies of ethylene and acetylene to form classical carbocations is equal to the energy change for the reaction

$$H_3C\text{–}CH_2^+ + HC{\equiv}CH \rightarrow H_2C{=}CH_2 + H_2C{=}CH^+ \tag{10}$$

Equation 10 then differs from eq 8 by only the ionization of the two radicals in eq 8, so the near thermoneutrality of eq 8 again makes the energy change for eq 10 almost exactly equal to the difference in the ionization potentials of ethyl and vinyl radicals.

For the same reason that vinyl radical is a better electron acceptor than ethyl radical, it is harder to remove an electron from the former than from the latter. The difference in ionization potentials is given by the energy of the reaction

$$H_2C{=}CH^\bullet + C_2H_5^+ \rightarrow H_3C\text{–}CH_2^\bullet + C_2H_3^+ \tag{11}$$

When the carbocations that are formed are classical, we calculate the difference in ionization potentials to be 4.5 kcal/mol[28] and the difference in proton affinities of ethylene and acetylene to be 5.4 kcal/mol.

However, the latter number should not be compared with the experimental difference of 9.3 kcal/mol between the gas-phase proton affinities of ethylene and acetylene,[29] since calculations that include electron correlation predict that both carbocations are "nonclassical", with one hydrogen occupying a bridging position equidistant from each carbon.[15b,18a,30]

At the CI-SD/6-31G** level, we find the hydrogen-bridged ethyl cation to be 3.7 kcal/mol more stable than the "classical" ethyl cation, but we find the hydrogen-bridged vinyl cation to be only 0.6 kcal/mol more stable than its "classical" counterpart. In fact, without correction for zero-point energy differences, unbridged vinyl cation is computed at the CI-SD/6-31G** level to be 0.2 kcal/mol more stable than the bridged ion. Higher level calculations give an energy difference between classical and bridged vinyl cations that is roughly 2.5 kcal/mol larger,[18a] but calculations at this higher level find hydrogen bridging in the vinyl cation still to be about 3 kcal/mol less stabilizing than in the ethyl cation.[15b] The 3.1 kcal/mol greater stabilization that we calculate to be provided by hydrogen bridging in the ethyl cation increases the calculated difference, represented by eq 11, between the adiabatic ionization potentials of vinyl and ethyl radicals to 7.6 kcal/mol.

Experimentally, the best value for the adiabatic ionization potential of the ethyl radical appears to be 187.2 kcal/mol.[15b] The value measured for the vinyl radical is 198.1 kcal/mol,[31] but the experimenters state that the low Franck–Condon factor associated with the transition from the unbridged geometry of the vinyl radical to the bridged geometry of the vinyl cation may have resulted in the 0 → 0 band not being observed. They further note that an adiabatic IP of about 195 kcal/mol is required if the vinyl C–H BDE at 0 K is 110 kcal/mol, the current experimental value for this BDE.[17,18] Taking 195 kcal/mol as the experimental adiabatic IP of vinyl radical, this IP exceeds that of ethyl radical by about 8 kcal/mol.

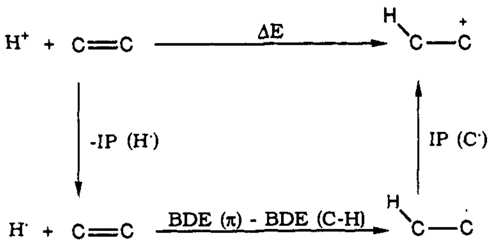

**Figure 1.** Thermocycle for analyzing the energy change, $\Delta E$, on protonation of a $\pi$ bond in terms of differences in IPs and BDEs.

Our calculated difference of 7.6 kcal/mol between the IPs of vinyl and ethyl radicals is in excellent agreement with an 8 kcal/mol difference between the experimental values. Moreover, our calculated difference of 8.5 kcal/mol between the proton affinities of ethylene and acetylene to form, respectively, hydrogen-bridged ethyl and vinyl cations, is also in good agreement with the difference of 9.3 kcal/mol between the measured proton affinities in the gas phase.[29]

In solution differential solvation effects selectively stabilize vinyl cations,[32] so that some alkynes undergo protonation almost as rapidly as the corresponding alkenes and in a few cases, even more rapidly.[33] Nevertheless, alkynes are usually somewhat less reactive toward protonation in solution than comparable alkenes—a result that has been attributed to the fact that the empty p orbital in a vinyl carbocation belongs to an sp rather than to an $sp^2$-hybridized carbon, and that the more electronegative sp-hybridized carbon is less tolerant of a positive charge.[1,34]

*Provided that carbocation stabilities are defined relative to the corresponding radicals*, this type of argument is essentially correct. The proton affinity of a $\pi$ bond is the negative of $\Delta E$ for the thermocycle shown in Figure 1. By using this thermocycle,

$$-\Delta E = \mathrm{IP}\ (H^\bullet) - \mathrm{BDE}\ (\pi) + \mathrm{BDE}\ (C\text{–}H) - \mathrm{IP}\ (C^\bullet) \tag{12}$$

Thus, the difference between the proton affinity of an alkene and an alkyne is equal to the difference in the C–H BDEs between tetrahedral and trigonal carbons, minus the difference in alkene and alkyne $\pi$-bond energies, minus the difference in ionization potentials between ethyl and vinyl radicals. As discussed above, the near thermoneutrality of eq 8 results in the difference in proton affinities being almost completely attributable to the difference in ionization potentials between ethyl and vinyl radicals. Thus, the greater ease of formation of ethyl cation from ethyl radical, as compared to vinyl cation from vinyl radical, may be viewed as being wholly responsible for the greater proton affinity of the prototypical alkene compared to the prototypical alkyne.

However, although radicals may be involved in the thermocycle in Figure 1, used to analyze the protonation of alkenes and alkynes, radicals are not involved in the actual protonation reactions. Protonation of a $\pi$ bond simply involves breaking that $\pi$ bond and forming a new C–H bond.

The energy of the C–H bond formed is just equal to the sum of the proton affinity, $-\Delta E$, and the BDE of the $\pi$ bond that is broken. Equation 12 shows that this sum is

$$-\Delta E + \mathrm{BDE}\ (\pi) = \mathrm{IP}\ (H^\bullet) + \mathrm{BDE}\ (C\text{–}H) - \mathrm{IP}\ (C^\bullet) \tag{13}$$

Therefore, the difference between the strengths of the C–H bonds formed by protonation of acetylene and ethylene is equal to the difference in homolytic C–H BDEs between trigonal and tetrahedral carbons minus the difference in the adiabatic ionization

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[28] It is interesting to note that, linearization of the vinyl radical, which places the unpaired electron in a pure p orbital, is calculated to require 4.7 kcal/mol. Thus, when classical carbocations are formed, the ionization potential of a linear vinyl radical is essentially the same as that of the ethyl radical. Consequently, it seems reasonable to attribute the difference between the ionization potentials calculated by using the equilibrium geometries of the vinyl and ethyl radicals to the difference in the hybridization of the singly occupied orbitals at these geometries.

[29] Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

[30] For a brief review of hydrogen bridging in protonated acetylene and ethylene, see ref 7, pp 383–85.

[31] Berkowitz, J.; Mayhew, C. A. Ruscic, B. *J. Chem. Phys.* **1988**, *88*, 7396.

[32] Lucchini, V.; Modena, G. *J. Am. Chem. Soc.* **1990**, *112*, 6291.

[33] Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.

[34] In the transition state for carbocation formation, the lower energy of the HOMO of acetylene compared to that of ethylene may contribute to the greater ease of protonation of ethylene.[27] Of course, the lower energy of the acetylene HOMO is not unrelated to the greater strength of the acetylene $\pi$ bond.

potentials between vinyl and ethyl radicals.[35] The C–H bond formed by protonation of acetylene is calculated to be 6.6 kcal/mol stronger that the C–H bond formed by protonation of ethylene when classical carbocations are generated, and 3.5 kcal/mol stronger when both carbocations are bridged.

The energetic cost of breaking a $\pi$ bond in acetylene is 12.0 kcal/mol greater than the cost of breaking the $\pi$ bond in ethylene. Thus, the difference between the strengths of the $\pi$ bonds that are broken on protonation of acetylene and ethylene exceeds that between the C–H bonds that are made, regardless of whether bridged or classical ions are formed. This analysis reveals that *the greater proton affinity of ethylene is not due to the greater stability of the carbocation formed on protonation, but to a weaker $\pi$ bond that is broken.*[34]

The same type of analysis shows that, in contrast to the addition of $H^+$, the addition of $H^-$ to acetylene is more exothermic than to ethylene by 25.8 kcal/mol, because the 12.0 kcal/mol greater strength of the $\pi$ bond in acetylene is overwhelmed by the combination of the greater thermodynamic stability of the C–H bond formed and of the lone pair of electrons in vinyl anion compared to ethyl anion. Of the 37.8 kcal/mol greater stabilization calculated for the vinyl anion, 11.1 kcal/mol is due to the greater homolytic BDE of the vinyl C–H bond, and 26.7 kcal/mol is due to the greater electron affinity of the vinyl radical.

When ethyl and vinyl carbanions or carbocations are formed by C–H bond cleavage instead of by addition of $H^-$ or $H^+$ to $\pi$ bonds, the relative $\pi$-bond energies of ethylene and acetylene are, of course, no longer relevant to the relative energetics of the reactions. Only the differences in homolytic C–H BDEs and electron affinities or ionization potentials determine the relative stabilities of the ions formed.

For example, in forming vinyl and ethyl anions by proton loss, the 11.1 kcal/mol greater energetic cost of homolytically cleaving a C–H bond in ethylene, compared to ethane, is overwhelmed by the 26.7 kcal/mol greater electron affinity of vinyl radical compared to ethyl radical. Thus, we calculate the exothermicity of the proton-transfer reaction

$$H_3C\text{–}CH_2^- + H_2C{=}CH_2 \rightarrow H_3C\text{–}CH_3 + H_2C{=}CH^- \quad (14)$$

to be 15.6 kcal/mol. Since ethyl anion is apparently not bound, the difference in gas-phase basicities between ethyl and vinyl anions has not been measured directly, but it has been estimated that protonation of ethyl anion should liberate about 15 kcal/mol more energy than protonation of vinyl anion.[24]

For formation of ethyl and vinyl cations by hydride abstraction, to the 11.1 kcal/mol greater homolytic C–H BDE of ethylene is added the 7.6 kcal/mol greater adiabatic IP of the vinyl radical. Thus, we calculate the hydride abstraction reaction

$$H_3C\text{–}CH_2^+ + H_2C{=}CH_2 \rightarrow H_3C\text{–}CH_3 + H_2C{=}CH^+ \quad (15)$$

to be endothermic by 18.7 kcal/mol.

The calculated energy change on equilibrating ethyl and vinyl cations by hydride abstraction, as in eq 15, instead of by proton transfer between $\pi$ bonds, as in eq 10, amounts to 10.2 kcal/mol. This is the same calculated energy change associated with equilibrating ethyl and vinyl anions by proton transfer, as in eq 14, instead of by hydride exchange between $\pi$ bonds, as in eq 9. The constancy of this difference between the two pairs of related reactions derives from the fact that, on subtracting either eq 14 from eq 9 or eq 15 from eq 10, eq 3 is obtained. This equation gives the difference between the heat of hydrogenation of acetylene and that of ethylene, which we calculate to be 10.2 kcal/mol, and for which the experimental value is 9.4 kcal/mol.

Generally, the ease of generating vinylic carbocations, carbanions, and radicals, compared to their alkyl counterparts, will depend on whether these intermediates are formed by additions to $\pi$ bonds or by cleavage of $\sigma$ bonds. The difference between the relative difficulty of generating vinyl and alkyl intermediates will increase by the difference between the alkyne and alkene hydrogenation energies. The dependence of relative ease of formation on mode of generation has significant consequences for the chemistry of vinylic versus alkyl radicals and vinylic versus alkyl carbocations.[36]

As discussed above, these two types of radicals are formed with nearly equal ease by $\pi$-bond addition reactions,[21,22] but formation by homolytic C–H bond cleavage is found to require considerably more energy for a vinylic[17] than for an alkyl[15] radical. Similarly, although formation of a vinylic carbocation by $\pi$-bound protonation is generally found to be slightly more difficult in solution than formation of a comparable alkyl cation,[1,33] the difference between the requirements for formation of the two types of carbocations by cleavage of a $\sigma$ bond to carbon is found to be considerably greater. This accounts for the relative difficulty in forming vinylic cations by cleavage of $\sigma$ bonds, rather than by protonation of triple bonds.[1,37]

## Conclusions

Our CI-SD calculations reveal that dissociation of a $\pi$ bond in acetylene requires 12.0 kcal/mol more energy than dissociation of the $\pi$ bond in ethylene. We calculate that hydrogenation of acetylene is, nevertheless, 10.2 kcal/mol more exothermic than hydrogenation of ethylene because the strengths of each of the two C–H bonds formed is computed to be 11.1 kcal/mol larger in ethylene than in ethane.

Because of the near equality of the difference between the $\pi$ BDEs of acetylene and ethylene and the difference between the C–H BDEs of ethylene and ethane, the energy difference between the addition of a hydrogen atom to acetylene and to ethylene is calculated to amount to only 0.9 kcal/mol. This near cancellation results in the calculated energy difference between hydride addition to acetylene and ethylene being nearly equal to the 26.7 kcal/mol that we compute for the energy difference between the electron affinities of the vinyl and ethyl radicals. Similarly, the calculated difference between the proton affinities of ethylene and acetylene is nearly the same as the 7.6 kcal/mol that we compute for the difference between the adiabatic ionization potentials of the ethyl and vinyl radicals.

The differences between the energies required to generate ethyl and vinyl radicals, anions, and cations depends on whether these species are formed by $\pi$-bond addition reactions or by cleavage of C–H $\sigma$ bonds. Compared to ethyl, the energy required to form each vinyl species is greater when it is formed by C–H bond cleavage than when it is formed by $\pi$-bond addition. We have shown that this increase in the relative energy required to form each vinyl species is equal to the difference between the heats of hydrogenation of acetylene and ethylene.

Quantitatively, the CI-SD/6-31G** energies for the reactions that we have calculated are in very good agreement with experiment. The very good agreement with experiment can be attributed to the fact that, instead of computing absolute energies, we have used isodesmic reactions to compute differences between strengths of bonds, ionization potentials, and electron affinities. Qualitatively, our results provide insights into the differences between the energetics of the addition reactions that double and triple bonds undergo with radicals, nucleophiles, electrophiles, and molecular hydrogen.

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(35) This is readily seen if to Figure 1 is added a separate step in which the $\pi$ bond is first broken to form a diradical. The negative of the energy change on protonating this diradical to form a carbocation is given by IP (H$^\bullet$) + BDE (C–H) – IP (C$^\bullet$), which is equal to the energy of the bond formed to the proton.

(36) If the addition of a nucleophile to a triple bond is fully 26 kcal/mol more exothermic than addition to a double bond, as in eq 9, the approximately 10 kcal/mol smaller difference between the ease of forming the two carbanions by deprotonation may have little qualitative effect on the chemistry observed.

(37) Reviews: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979. Rappoport, Z. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press, New York, 1983; Vol. 3, pp 427–615.

Center for a generous allocation of computer time and Dr. David Hrovat for his help.

## Appendix: A Critique of Obtaining $\pi$ BDEs from Adiabatic C–C BDEs

As noted in the introduction, the hypothesis that breaking a $\pi$ bond in acetylene requires less energy than breaking a $\pi$ bond in ethylene appears to find support in the comparison of the energies required to dissociate acetylene to two molecules of CH ($^2\Pi$), ethylene to two molecules of $CH_2$ ($^3B_2$), and ethane to two $CH_3$ radicals.[1,2] Recent experimental values for these adiabatic C–C bond dissociation energies (BDEs) are, respectively, 229 kcal/mol,[17] 171 kcal/mol,[17] and 89 kcal/mol.[38] These BDEs give a difference of 58 kcal/mol between the strengths of the C–C triple bond in acetylene and the C–C double bond in ethylene. This difference is, indeed, less than the difference of 82 kcal/mol between the strengths of the C–C double bond in ethylene and the C–C single bond in ethane.

There are, however, some problems associated with assigning these differences in adiabatic C–C BDEs entirely to $\pi$-bond strengths. For example, since the hybridization of the carbons in each of these three molecules is different, one would expect the strengths of the C–C $\sigma$ bonds also to differ. Indeed, the C–H BDE in ethylene[17] is about 11 kcal/mol larger than that in ethane,[15] so that it would be very surprising if the C–C $\sigma$ bond between the nominally $sp^2$-hybridized carbons in ethylene were not also considerably stronger than that between the nominally $sp^3$ carbons in ethane. A greater strength for the C–C $\sigma$ bond in ethylene accounts, at least in part,[40] for the fact that the difference of 82 kcal/mol between the C–C BDEs of ethylene and ethane exceeds the experimental value of 64–65 kcal/mol for the strength of the $\pi$ bond in ethylene.[13,14]

Since the C–H BDE in acetylene exceeds that in ethylene by about 21 kcal/mol,[17] there is every reason to believe that the C–C $\sigma$ bond between the nominally sp carbons in acetylene is even stronger than that between the nominally $sp^2$ carbons in ethylene. Thus, one might conclude that the energy necessary to break one $\pi$ bond in acetylene is considerably less than the difference of 58 kcal/mol between the adiabatic C–C BDEs of acetylene and ethylene.

This conclusion would be incorrect because the adiabatic BDE of acetylene contains a contribution from the difference between the electronic configurations of the CH groups in acetylene and in the ground state of the two CH molecules formed from it upon C–C cleavage. In acetylene, the C–C bonds are formed by each CH group contributing one $\sigma$ and two $\pi$ electrons, and diabatic dissociation of acetylene would lead to two CH molecules with the same electronic configuration. However, the resulting $^4\Sigma$ state is not the ground state of CH, but lies 16.7 kcal/mol above it.[41] The $^2\Pi$ ground state has two $\sigma$ and only one $\pi$ electron. Thus, demotion of an electron from a $\pi$ to a $\sigma$ orbital in going from acetylene to the ground state of each CH molecule reduces the adiabatic C–C BDE in acetylene by 33.4 kcal/mol. The diabatic C–C BDE of acetylene to two $^4\Sigma$ CH molecules, in which the electronic configuration of the CH groups remains the same, provides a purer measure of the intrinsic strength of the C–C triple bond.[42]

The diabatic C–C BDE of acetylene is 33.4 kcal/mol greater than the adiabatic C–C BDE of 229 kcal/mol. In contrast, since ethylene dissociates diabatically, as well as adiabatically, to the two $^3B_2$ $CH_2$ molecules, its diabatic and adiabatic C–C BDEs are the same, 171 kcal/mol. Thus, the diabatic C–C BDE of acetylene exceeds that of ethylene by about 91 kcal/mol. As in the comparison of the C–C BDEs of ethylene and ethane, the difference of 91 kcal/mol between the diabatic C–C BDEs of acetylene and ethylene contains contributions from both $\sigma$ and $\pi$ bonds.

Finally, it should be noted that in the $^3B_2$ state of $CH_2$, there are two unpaired electrons that are correlated by the Pauli exclusion principle. In the $^4H$ state of CH, three unpaired electrons are correlated pairwise. This correlation is not present to the same extent in these fragments in the molecules from which each is formed. This additional electron correlation in the dissociation products formed when multiple C–C bonds are broken will result in the BDE of ethylene to $^3B_2$ $CH_2$ and that of acetylene to $^4\Sigma$ CH each being less than the sum of the separate strengths of the individual $\sigma$ and $\pi$ bonds that each molecule contains.

Extracting $\pi$ BDEs from differences between C–C BDEs in molecules containing different numbers of $\pi$ bonds is obviously not at all straightforward. Therefore, obtaining directly the energies required to break $\pi$ bonds, either from activation energies[13] or from thermodynamic measurements,[14] is certainly to be preferred.[43]

**Registry No.** $HC{\equiv}CH$, 74-86-2; $H_2C{=}CH_2$, 74-85-1; $H_2C{=}CH^{\bullet}$, 2669-89-8; H, 12385-13-6; $H^{\bullet}$, 12184-88-2; $H_3CCH_2^-$, 2025-56-1; $C_2H_3^+$, 14604-48-9; $C_2H_5^+$, 14936-94-8; $C_2H_3^-$, 25012-81-1; $C_2H_5^-$, 25013-41-6.

**Supplementary Material Available:** Optimized geometries in *Z* matrix format (4 pages). Ordering information is given on any current masthead page.

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[38] Based on a heat of formation for the methyl radical of $\Delta H_f^\circ = 34.4$ kcal/mol at 298 K[39] and the heat of formation of ethane at the same temperature.[12]

[39] Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

[40] The $\pi$ radical centers in two molecules of $^3B_2CH_2$ are not stabilized by hyperconjugation, whereas those in twisted ethylene and in two ethyl radicals are. This disparity also contributes to making the difference between the C–C BDEs of ethylene and ethane larger than the $\pi$-bond strength that is obtained from either the energy required for cis-trans isomerization of ethylene or ethyl radical disproportionation (eq 4).

[41] Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

[42] A similar situation obtains in tetrafluoroethylene. The diabatic BDE to two molecules of $^3B_2$ $CF_2$ provides a better measure of the intrinsic strength of the C–C double bond than does the adiabatic BDE to two molecules of $CF_2$ in its $^1A_1$ ground state, where the nonbonding electrons both occupy a $\sigma$ orbital. Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1986**, *90*, 998.

[43] For another approach to obtaining $\pi$ BDEs, see: Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.