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Heats of Hydrogenation and Formation of Linear Alkynes and a Molecular Mechanics Interpretation[1]

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Abstract: The heats of hydrogenation of all of the isomeric linear alkynes containing from six to ten carbons have been measured in hexane solution at room temperature. They were found to be systematically larger by about 4 kcal when the triple bond is at the end of the chain. For the remaining isomers, the heat of hydrogenation decreases further slightly and monotonically as the triple bond moves from the 2 position toward the center of the chain. This result is interpreted in terms of the conformational mixture present with the aid of molecular mechanics calculations.

The thermochemistry of linear monoalkynes is a good deal more interesting than its sparse literature[3-5] would indicate. The simple picture of a triple bond as two orthogonal ethylene-like π bonds is inadequate on thermochemical grounds alone. Twice the heat of hydrogenation of ethylene (−32.32 kcal/mol)[6] does not yield the heat of hydrogenation of acetylene (−75.06 kcal/mol)[3] and our present results show that a similar inequality holds for all linear alkynes up to and including the decynes. Moreover, Dewar[7] has pointed out that triple bonds do not behave chemically as double bonds do, e.g., in their inability to add bromine under mild conditions; nor is their electron affinity comparable to that of the olefins.[8] For a review, see ref 9.

The stability of a triple bond is known to vary with its location in the chain.[9-13] Isomerization can be brought about by treatment with base under suitable conditions. Thus, with potassium hydroxide at 175 °C, 2-pentyne is found to predominate over the 1 isomer in a ratio of 7:3.[11] Such an isomerization takes place via the allene,[11] and there is a certain amount of allene in equilibrium with the alkynes under basic conditions.[11,14] The amount of allene is small in the case of open-chain compounds,[11,14] but may be sizable with macrocyclic molecules.[15,16] The conjugated diene is even more stable, but it is more slowly formed, and rarely detected.[15] If a very strong base is used in the equilibration, such as sodamide, it will react with the 1-alkyne to give the salt.[12] The equilibrium is thus shifted by removal of the alkyne as the salt, and treatment with sodamide is a standard method for the isomerization of an acetylene to the corresponding 1-alkyne.[12] Equilibration studies on alkynes have been carried out, but the results are difficult to interpret. It would appear, at least under some conditions, that the more centrally located triple bond predominates over the less centrally located one. However, other reactions are going on which are destroying the alkynes, and it is unclear whether or not equilibrium is actually ever reached.

If we consider a series of alkynes, all of which can be reduced to the same alkane, the relative heats of formation are given directly by the relative heats of hydrogenation. Since the absolute heats of formation of the alkanes are generally known,[17] the heats of formation of the alkynes can be found.

While heats of hydrogenation in the gas phase

$$C_nH_{2n-2}(g) + 2H_2(g) = C_nH_{2n+2}(g)$$

would be most desirable, they have not been measured directly at 25 °C, because the alkynes in question are liquids in the standard state and the higher homologues are not even very volatile. Since Williams' early paper on hydrogenation in the liquid phase,[18] it has been clear that this is the method of choice for hydrocarbons of more than, say, five carbon atoms, for reasons of experimental feasibility. The heats of hydrogenation of alkynes in hexane solution are certainly not identical with the gas-phase values but, in the absence of the necessary heats of solution and vaporization, we estimate that they are very close, probably within experimental error. In effect, we are saying that the reaction producing an essentially infinitely dilute solution of reaction product in hexane

$$C_nH_{2n-2}(7\% \text{ in hexane}) + 2H_2(g) = C_nH_{2n+2}(\text{v dil})$$

is not thermochemically different from the gas-phase reaction above. This is reasonable on the qualitative grounds that separation of alkyne molecules from one another by going from

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the pure liquid to the gas (vaporization) is energetically comparable to sepration of alkyne molecules by inert solvent to form the relatively dilute reactant solution in the same way that vaporization of the alkane is energetically comparable to separation of product alkane molecules to form the very dilute product solution. The only substantial energetic effect which might be superimposed on the heat of hydrogenation is the heat of dilution of the 7% alkyne solution in hexane to a very dilute solution of the hydrogenation product, also in hexane. Because of its use as a thermochemical standard, we must make the same assumptions with regard to the hydrogenation of hexene as we make with regard to the alkyne reaction: that there be no substantial energetic difference between the reaction in dilute hexane solution and the gas-phase reaction. While we believe that these assumptions regarding the reaction in hexane solvent vs. the gas phase are good ones, even the little error which does result will be largely canceled out when the alkyne is compared with the standard 1-hexene.

We do not have any combustion data on the higher linear alkynes for comparison and testing of these assumptions but we can compare the heats of hydrogenation of some terminal alkenes, determined by direct hydrogenation, with the corresponding values determined indirectly from heats of combustion. Taking −30.25 kcal/mol[19] as the heat of hydrogenation of 1-hexene in the gas phase (not −29.56 kcal/mol as was erroneously used in the original paper[20a]), one has −30.28, −30.25, −30.04, −30.35, and −30.33 kcal/mol for the heats of hydrogenation of the C_6 to C_{10} terminal alkenes[20a] measured directly. The mean of these experimental means is −30.27 kcal/mol. The mean standard deviation over all 50 experimental runs is 0.30 kcal/mol and the standard deviation of the experimental means about their grand mean is 0.13 kcal/mol.

Heats of hydrogenation of the C_6 to C_{10} alkenes calculated indirectly from their heats of combustion in the gas phase and those of their hydrogenation products are −30.17, −30.35, −30.45, none available for C_9, and −30.16 kcal/mol. The mean is −30.28 kcal/mol and the mean combined uncertainty of the heats of formation of hydrogenation reactants and products is 0.58 kcal/mol. Agreement between direct and indirect measurements is well within the combined uncertainties indicating that there are no experimentally noticeable solvent effects for hydrogenation of 10% solutions of the C_6 to C_{10} terminal alkenes in hexane.

Experimental Section

Apparatus. The calorimeter has been described at various phases of its evolution.[20] At present, it consists of a 25-mL Erlenmeyer flask fitted with a soft rubber serum bottle stopper through which a 2-kΩ steel-jacketed thermistor probe (Cole-Parmer 8436) and a hydrogen inlet needle are inserted. The flask contains 20 mL of *n*-hexane along with 0.6 g of 10% Pd catalyst on charcoal support, and the suspension is magnetically stirred. After a 15-30-min activation time, 40-μL samples of alkynes in *n*-hexane solution were injected into the hexane-catalyst slurry through the portion of the serum bottle stopper not occupied by the thermistor probe and hydrogen inlet. The hydrogen valve was left open throughout the entire set of runs to maintain constant pressure at about 2 atm. If a hydrogen leak occurs, it makes itself evident through a continuous and marked temperature drop due to evaporation of the calorimeter fluid. The calorimeter was operated at room temperature of about 25 °C and was shielded from ambient temperature changes by a styrofoam insulating well of about 3-cm thickness on all sides and the bottom but open at the top.

The thermistor leads were connected as the unknown arm of a conventional dc Wheatstone bridge circuit consisting of two 1.8-kΩ metal film resistors as the constant arms of the bridge and a 10-kΩ switch resistance box as the adjustable arm. The bridge was powered by a 6-V dry battery moderated by another 10-kΩ resistance box usually set at 1000-2000 Ω. A potentiometric recorder was connected across the bridge in place of a null device to determine the degree of bridge imbalance. The potentiometer registered full-scale deflection (25 cm) for a 1-mV potential change. At these small changes in bridge output voltage, thermistor and bridge response are essentially linear with temperature so that the potentiometer deflection during hydrogenation is directly proportional to the heat of reaction.

Reagents. All alkynes were obtained from Chemical Samples Co., Columbus, Ohio, and are guaranteed to be 99% pure or better. The exception is 5-decyne, which is 98% or better. In view of the difficulty of separating 3- and 4-decyne from 5-decyne, positional isomers probably constitute the major impurity in 5-decyne. The 5-decyne sample was found to be homogeneous to GLC analysis on a 100-ft SE-30 capillary column using a hydrogen flame ionization detector. Decane, 1-decyne, and 2-decyne all separated very cleanly from the 5 isomer using this column at 85 °C but the 3-, 4-, and 5-decynes gave a single serrated peak. Because both the 3- and 4-decynes have heats of hydrogenation which are very close to that of 5-decyne; the thermochemical purity of the sample, as contrasted to its isomeric purity, is probably much higher than 98%. The same can be said for any alkyne contaminated with its own positional isomers except, perhaps, when the 1-alkyne is involved. This is so because 1-alkynes have substantially higher heats of hydrogenation than the rest; but it is also true that they are easier to separate from their positional isomers than alkynes with internal triple bonds, hence contamination by 1-alkynes is probably the least likely kind.

Reagent grade *n*-hexane from J. T. Baker was used as a solvent inert to hydrogen in making up the samples and as the calorimeter fluid. Pd catalyst on charcoal (10%) was obtained from Englehard Industries, Newark, N.J. 1-Hexene was used as a thermochemical standard in much the same way that benzoic acid is used in combustion calorimetry. It was supplied in 99.9% purity by Chemical Samples Co. The heat of hydrogenation of 1-hexene in the liquid state was taken to be −30.25 kcal/mol.[19]

Procedure. After 600-700 mg of alkyne was weighed out to ±0.1 mg, a 10.00-mL solution was made up to the mark with *n*-hexane. Having an anticipated ΔH_{H_2} to work from, it was an easy matter to compute the number of moles of hexene which would be thermochemically equivalent to the unknown, to within a few percent. If we do not have an anticipated result, a rough preliminary run with any known hexene standard achieves the same end. The rest of the experiment is devoted to removing as much of the remaining few percent uncertainty as possible.

Upon injection of a 40-μL sample by means of a microliter syringe, the recorder trace represents a typical temperature vs. time curve with the temperature variation being in parts of a millivolt. Alternating injections of standard and sample yield curves which may be extrapolated in the usual way[21] to obtain an idealized vertical temperature rise. The ratio of temperature rise per millimole was then substituted into the equation

$$\frac{(\Delta T/\mathrm{mM})}{-30.25} = \frac{(\Delta T'/\mathrm{mM}')}{\Delta H_{H_2}}$$

to give the unknown ΔH_{H_2}.

Nine aliquot portions of standard were measured in alternation with nine of unknown to yield nine ratios of temperature rise of unknown to that of sample, $\Delta T'/\Delta T$. These permitted calculation of the arithmetic mean ΔH_{H_2}, which constitutes an entry in Table I. The uncertainties are 95% confidence limits for eight degrees of freedom or $0.77\ \sigma = \mathrm{CL}_{95}$.

After a series of reactions had been run, the calorimeter fluid was subjected to GLC analysis using an *SE*-30 capillary column. No GLC analysis revealed traces of unreacted alkyne or alkene, although experiments with intentionally contaminated samples showed that separation is excellent and sensitivity is very good for trace unsaturation.

Results and Discussion

The heats of hydrogenation in the liquid phase of all linear alkynes from C_2 to C_{10} are shown in Table I. Two cross-checks can be made between the thermochemical literature and the experimental results reported here. Turner[5] obtained −62.8 kcal/mol for the heat of hydrogenation of 4-octyne in glacial acetic acid. The experimental procedure involved breaking a sealed ampule of reactant into the calorimeter fluid, which produced a heat of solution. After thermal equilibrium had been reestablished, another ampule, this one containing catalyst, was broken into the solution and the temperature rise due

Table I. Heats of Hydrogenation of the Linear Alkynes to C_{10}[a,b]

compd	1-	2-	3-	4-	5-
acetylene	−75.06 (0.16)[3] −74.03				
propyne	−69.70 (0.03)[3] −69.63				
butyne	−69.85[4] (0.25) −69.50	−65.58 (0.32)[3] −65.54			
pentyne	−69.50 (0.70)[31] −69.26	−65.80 (0.70)[31] −65.30			
hexyne	−69.16 (0.11) −69.15	−65.65 (0.40) −65.08	−65.11 (0.28) −65.11		
heptyne	−69.65 (0.39) −69.03	−65.11 (0.31) −64.95	−64.63 (0.36) −64.87		
octyne	−69.15 (0.62) −68.98	−65.10 (0.11) −64.82	−64.80 (0.19) −64.74	−64.22 (0.26) −64.63	
nonyne	−69.54 (0.46) −68.98	−65.08 (0.51) −64.77	−64.69 (0.34) −64.62	−64.69 (0.43) −64.51	
decyne	−69.65 (0.51) −68.97	−65.27 (0.51) −64.77	−64.86 (0.47) −64.56	−64.39 (0.41) −64.39	−64.10 (0.47) −64.37

[a] Upper entries are experimental values; lower entries are calculated by molecular mechanics. Literature values are indicated by references with superscripts in the usual way. If no reference is indicated, the value was determined in the present work. [b] Numbers in parentheses indicate 95% confidence limits on present experimental results or estimated 95% confidence limits on literature values.

to hydrogenation of both catalyst and sample was observed. In a separate experiment, an ampule of catalyst was broken in a calorimeter set up exactly as the first had been except that it contained no sample. The heat of activation of the catalyst obtained from the second experiment was subtracted from the total heat observed in the first yielding the heat of hydrogenation of the sample by difference. This experimental strategy was no doubt arrived at to avoid the heat of solution contribution to the observed heat which would have resulted had the order of braking of the ampules been reversed but it does not entirely achieve that end. Alkenes, being Lewis bases, react with glacial acetic acid exothermically but alkanes do not. This acid-base pair is broken up during hydrogenation of an alkene (or an alkyne) to the corresponding alkane. It is this endothermic dissociation which we believe causes Turner's results to be less exothermic than those of other groups.

Another approach to heats of solution in glacial acid hydrogenation is that taken by Williams,[18] Skinner,[22] and, in early work, by our group.[23] These three groups determined the heat of hydrogenation with catalyst already present as a slurry in the acid, then corrected the results for the heat of solution of the reaction product determined in a separate experiment. In the present case, the heat of solution of octane in acetic acid is the value of interest[23] for which Skinner obtained 1.5 kcal/mol and for which we found an approximate value of 1.3 kcal/mol. If these endothermic correction factors are subtracted from Turner's value for ΔH_{H_2} of 4-octyne one obtains −64.1 and −64.3 kcal/mol, which bracket the value for hydrogenation in hexane solution given in Table I. This coincidence suggested that the heats of solution of alkynes in acetic acid might be near zero. There is anticipated an exothermic contribution from the acid-base reaction, and an endothermic contribution from the disruption of the acetic acid liquid structure, which might approximately cancel. Preliminary measurements on 4-octyne and octane showed, however, that our prediction was in the right direction but quantitatively wrong. We obtained 0.95 kcal/mol for the heat of solution of 4-octyne and a new (better) value of 1.67 kcal/mol for octane. The difference between these two values, 0.72 kcal/mol, is absorbed during the -yne -ane conversion in acetic acid. Hence Turner's corrected heat of hydrogenation value is −63.5 kcal/mol, which is lower than our value but within the combined experimental uncertainties.

The second cross-check between the literature and Table I is Skinner's value for the heat of hydrogenation of 1,7-octadiyne,[22] appropriately corrected for the heat of solution of octane, which is −139.7 kcal/mol. Since we do not anticipate conjugative or steric influence on a linear diyne with distant triple bonds, one-half Skinner's value should coincide with the experimental datum for 1-octyne in Table I, which it does, to within combined uncertainties.

The terminal alkynes are, clearly, much more energetic (enthalpic) than all of their isomers. Moreover, since all C_5 to C_{10} terminal alkynes are about equally exothermic on hydrogenation, the enthalpy of the triple bond is about the same for all of them. There is a sharp drop in the magnitude of the heat of hydrogenation of a triple bond in the 1 position to one in the 2 position followed by a small consistent decrease in ΔH_{H_2} as we proceed from the 2 position to the 5 position in decyne or the 4 position in nonyne and octyne. The combined confidence limits are, however, larger than the difference between ΔH_{H_2} for adjacent isomers so that the apparent negative slope could be a result of experimental scatter. The typical 95% confidence limits in Figure 1 show that one could draw a horizontal line from the lower confidence limit of 2-decyne to a point just above the upper confidence limit of 5-decyne without doing great violence to either statistics or the experimental data.

To obtain more quantitative evaluation of the data for the alkynes in the 2 to 5 positions, we calculated the statistical significance of the difference between ΔH_{H_2} for 2-decyne and 5-decyne. Following the method of Croxton[24] we wished to have the best estimator, $\hat{\sigma}_{\bar{X}_1-\bar{X}_2}$, of the standard deviation of the difference between two sample means, $\sigma_{\bar{X}_1-\bar{X}_2}$:

$$\hat{\sigma}_{\bar{X}_1-\bar{X}_2} = \sqrt{\frac{\hat{\sigma}_1{}^2 + \hat{\sigma}_2{}^2}{N_1 + N_2}}$$

$$= \hat{\sigma}_{1+2}\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}$$

where $\hat{\sigma}_{1+2}$ is the best estimator of the population standard deviation, σ, drawn from two sample means, $\bar{X}_1$ and $\bar{X}_2$. The best estimator $\hat{\sigma}_{1+2}$ is

$$\hat{\sigma}_{1+2} = \sqrt{\frac{\sum d_1{}^2 + \sum d_2{}^2}{N_1 - 1 + N_2 - 1}}$$

and is found to be 0.49 kcal/mol from the data for 2-decyne and 5-decyne in Table I.

The best estimator of the standard deviation of the mean

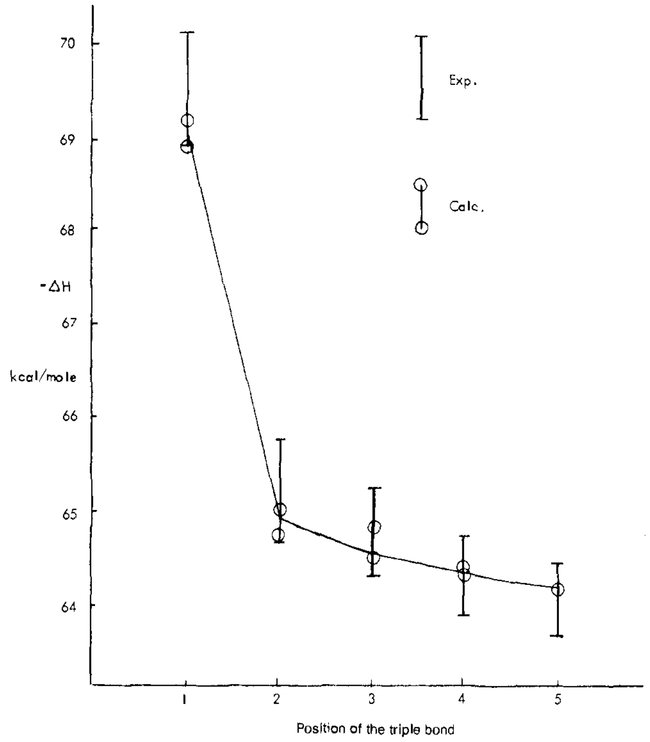

Figure 1. Heats of hydrogenation of the linear alkynes. The experimental range indicates CL_{95} for the decynes. The calculated range indicates the range of calculated values for each position except in the case of 5-decyne, for which there is only one calculated value.

(standard error) for the difference of the two sample means is

$$\hat{\sigma}_{\overline{X}_1-\overline{X}_2} = \hat{\sigma}_{1+2}\sqrt{\frac{1}{N_1}+\frac{1}{N_2}} = 0.231$$

for the two decynes selected. Calculating confidence limits for 16 degrees of freedom, we find that any difference in ΔH_{H_2} greater than 0.40 kcal/mol is statistically significant at the 90% confidence level, a difference >0.49 kcal/mol is significant at the 95% level, and one >0.68 kcal/mol is significant at the 99% level. The difference between 2-decyne and 5-decyne is significant at the 99% level or higher.

Since the number of hydrogenations is the same for all entries in the table ($N = 9$) and since the standard deviation of the means of 2-decyne and 5-decyne are about as high as can be found in the table, these criteria apply to the whole data set, not just to the two compounds selected for the calculation. The conclusion is that the negative slope in Figure 1 is real and not due to experimental error.

One might suppose that the data in Table I can be explained by a regular difference in the solvent effects for, e.g., 2-, 3-, 4- and 5-decyne, but we think that this is unlikely. Separating the actual reaction into two hypothetical parts, a dilution followed by a hydrogenation at (essentially) infinite dilution,

$$C_nH_{2n-2}(7\%) \rightarrow C_nH_{2n-2}(\mathrm{dil}) + H_2(g) \rightarrow C_nH_{2n+2}(\mathrm{dil})$$

the product, in the case of several positional isomers of an alkyne, is the corresponding alkane and is the same for all isomers. The only way solvent interactions could influence the final results would be through the first dilution step, an effect which would certainly be much smaller than the corresponding heat of vaporization and would arise as the result of significant differences in alkyne association among the positional isomers. Evidence that large differences in molecular association and volatility do not exist among positional isomers (exclusive of the 1 isomer) is one's inability to separate 3-, 4-, and 5-decyne by GLC using a 100-ft SE-30 capillary column.

The smaller acetylene molecules are, to some extent, special cases. But from the heptyne series through the decyne series, there are some clear generalizations that can be drawn from the observed heats of hydrogenation. The 1-alkynes (excluding acetylene) have a heat of hydrogenation which is 69.4 ± 0.3 kcal/mol. The 2-alkynes for the same group of compounds have heats of hydrogenation which are 65.4 ± 0.3 kcal/mol. The bulk of the difference (4.0 kcal/mol) is clearly due to a substituent effect (the replacement of a hydrogen by an alkyl). There may be other effects here also, which are not immediately obvious.

Again, looking at the same series of compounds, the 3-alkynes have heats of hydrogenation in the range of 64.8 ± 0.3 kcal/mol. Continuing along the series, we find that the 4-alkynes have heats of hydrogenation of 64.4 ± 0.3 kcal/mol, and the only example of a 5-alkyne has a heat of hydrogenation of 64.1 ± 0.5 kcal/mol. Hence, there is a clear trend, where the heat of hydrogenation of the triple bond is monotonically diminished as the bond moves from the end of the chain toward the middle of the chain.

To understand these data at the molecular level, we need to consider the following. In general, the alkynes being reduced, and the alkanes to which they are reduced, are mixtures of various conformations at room temperature, according to Boltzmann distributions. In order to find the extent to which the heat of formation is a function of structure, we must take into account the presence of these high-energy conformations, which influence the experimental heats of formation. Specifically, we might ask if the systematic change in the heat of hydrogenation through the series of 2- to 5-alkynes (Figure 1) is due to fundamental structural differences, or is it simply a result of differing amounts of the high-energy conformations, which happen to vary systematically with the location of the triple bond.

One of our objectives is to be able to reproduce trends in series of compounds such as are observed above with the aid of our molecular mechanics model.[25,26] The experimental heats of hydrogenation (Table I) give us the differences in the enthalpies between the alkyne and the corresponding alkane to which it is hydrogenated. Since we know rather accurately the heats of formation of the alkanes,[17] measurement of the heats of hydrogenation gives us the heats of formation of the corresponding alkynes (subject to previously discussed assumptions). One of the quantities which is calculable by molecular mechanics for a series of alkynes is the heat of formation. Such calculations were described previously using the 1973 force field (MMI program).[27] In the present work the calculations were updated using the 1977 force field[26] and utilizing in addition the experimental data for the larger alkynes as described in this paper.

We first attempted to fit the observed enthalpy data utilizing only two parameters as was previously done.[27] These were a bond energy parameter for the triple bond itself, and another bond energy parameter for a bond between an sp-hybridized carbon and an sp^3-hybridized carbon. (The Csp^3-Csp^3 and C-H parameters were previously evaluated for alkanes, and the same values are used here.) The calculated results failed to show the experimentally observed greater stability of the 3-yne relative to the 2-yne, but were otherwise reasonable.

It was found that these results could be improved by introducing a third parameter, which was a separate heat of formation increment for a methyl group attached to an sp-hybridized carbon. The physical rationale for this quantity is the same as that for introducing a special increment for a methyl attached to a carbon carrying a heteroatom, as we did with the sulfides,[28] alcohols,[29] amines,[30] etc. Namely, this is a defect in the van der Waals calculation for close nonbonded atoms,

Table II. Heats of Formation of Linear Alkynes (kcal/mol)

compd	T/R	POP	TORS	$\sum^a$	calcd ΔH_f° alkynes	calcd ΔH_f° alkanes[26]	exptl ΔH_f° (298) alkynes
acetylene	2.10	0.0	0.0	2.10	54.65	−19.38	54.34 (0.19)[17]
propyne	2.40	0.0	−0.36	2.04	44.86	−24.77	44.39 (0.21)[17]
1-butyne	2.40	0.0	0.0	2.40	39.65	−29.85	39.49 (0.21)[17]
2-butyne	2.40	0.0	−0.36	2.04	35.65		34.71 (0.20)[17]
1-pentyne	2.40	0.09	+0.36	2.85	34.36	−34.90	34.40 (0.85)[31]
2-pentyne	2.40	0.0	0.0	2.40	30.16		30.70 (0.85)[31]
1-hexyne	2.40	0.30	+0.72	3.42	29.18	−39.97	29.23 (0.29)
2-hexyne	2.40	0.09	+0.36	2.85	25.11		25.73 (0.58)
3-hexyne	2.40	0.0	+0.36	2.76	25.14		25.19 (0.46)
1-heptyne	2.40	0.52	+1.08	4.00	24.00	−45.03	24.80 (0.61)
2-heptyne	2.40	0.30	+0.72	3.42	19.92		20.26 (0.53)
3-heptyne	2.40	0.09	+0.72	3.21	19.84		19.78 (0.58)
1-octyne	2.40	0.82	+1.44	4.66	18.88	−50.30	19.29 (0.87)
2-octyne	2.40	0.52	1.08	4.00	14.72		15.24 (0.36)
3-octyne	2.40	0.30	1.08	3.78	14.64		14.94 (0.44)
4-octyne	2.40	0.18	1.08	3.66	14.53		14.36 (0.51)
1-nonyne	2.40	1.17	1.80	5.35	13.82	−55.16	14.88 (0.71)
2-nonyne	2.40	0.82	1.44	4.66	9.61		10.42 (0.72)
3-nonyne	2.40	0.52	1.44	4.36	9.46		10.03 (0.59)
4-nonyne	2.40	0.39	1.44	4.23	9.35		10.03 (0.68)
1-decyne	2.40	1.52	2.16	6.08	8.74	−60.23	10.01 (0.82)
2-decyne	2.40	1.17	1.80	5.37	4.54		5.63 (0.82)
3-decyne	2.40	0.82	1.80	5.02	4.33		5.22 (0.78)
4-decyne	2.40	0.62	1.80	4.82	4.16		4.75 (0.72)
5-decyne	2.40	0.59	1.80	4.79	4.14		4.46 (0.78)

[a] The quantities T/R, POP, and TORS are respectively the translation/rotation and *PV* contributions to the enthalpy at 25 °C, the "population increment", which increases the enthalpy by the amount shown owing to the presence of excited conformations, and the "torsional increment", which increases the enthalpy by virtue of the presence of relatively unhindered torsions.[25] (These lead to a compression of the torsional levels, relative to when the barrier is higher, which leads to a greater population of excited torsional levels. It is empirically found that 0.36 kcal mol^{-1}/low torsional barrier (excluding methyl groups which are already accounted for) is the optimum amount.) The sum of these three items is represented by the symbol Σ.

which is too small to show in the structural calculations, but which is detected in the energy calculation. Regardless of the physical interpretation applied, the fact is that with these other series of compounds a methyl group in CH_3X is thermochemically different from a methyl in a normal alkyl group in CH_3CH_2R, and to obtain the best results one needed a separate parameter. The same was found here also. The difference in this case is small, as might be supposed (Table III). After these parameters (Table III) were determined, calculated heats of formation were obtained (Table II) leading to heats of hydrogenation which are compared with the corresponding experimental quantities in Table I.

It was also found with other classes of compounds[25,28,30] that attachment of a heteroatom to a secondary or tertiary carbon required additional heat of formation increments. The same may well be true here, but insufficient data exist for us to evaluate this feature.

As the data in Table II show, there is a systematic calculated difference, with the 1-alkyne being much higher in energy (primarily because of the missing C–C bond increment), followed by the 2-alkyne, 3-alkyne, 4-alkyne, and 5-alkyne in that order. The reason for this trend, apart from the 1-alkyne, where there is also an actual bond difference, and the 2-alkyne, where there is also a methyl increment, is to be found in the population increment. If we take the decynes as an example, at room temperature each compound is a conformational mixture. The conformation of lowest enthalpy has all of the C–C bonds arranged anti to one another. There are various conformations possible where there is one gauche bond. There are other conformations where there are two gauche bonds, or more. These conformations with gauche bonds increase the enthalpy of the total mixture. The $T\Delta S$ term is, of course, in each case of such a magnitude as to minimize the free energy, but the enthalpy is increased. The amount by which it is increased depends on the energies of the various conformations, which are known from the calculations. In the butynes there is only one conformation corresponding to an energy minimum in each case. So no change in enthalpy results from this conformational mixing. This is also true for 2-pentyne, but for 1-pentyne there are gauche/anti isomers possible about the 3–4 bond. The gauche isomer has a relatively low heat content in this case, so its presence increases the heat content of the mixture by only 0.09 kcal/mol. (See the column headed POP (for population increment[25]) in the tables.) In 1-hexyne, gauche isomers are possible about the 3–4 bond, and also about the 4–5 bond. When this is worked out in full using a Boltzmann distribution, the increase in enthalpy is calculated to be 0.30 kcal/mol. For higher isomers the problem becomes complex, but in our calculation for the larger alkanes, the increase in enthalpy due to conformational mixing increases from a normal alkane to the next higher homologue by 0.35 kcal/mol.[25] As the alkyl chain becomes larger, the effect of the triple bond becomes negligible on the more distant part of the chain, and the same numerical limiting value would be reached. Hence for 1-heptyne we have added 0.22 kcal/mol to the value for 1-hexyne, and we have similarly added an increment of 0.30 to octyne, and then 0.35 to each successive 1-alkyne as we go up the homologous series.

Coming back to the 2-pentyne molecule, only one energy minimum is possible (the free rotation of the alkyl groups about the triple bonds not being physically meaningful). But for 2-hexyne, we again have a pair of gauche isomers, in addition to the anti isomer, as was found for 1-pentyne. The situation for the 2-alkynes is the same as for the 1-alkynes, but everything occurs one carbon further down the chain. Hence, we see the numbers (Table I) beginning with 2-pentyne, and followed by

Table III. Molecular Mechanics Parameters[a]

atom	r^*, Å	ϵ, kcal mol^{-1}
C[b]	1.94	0.044
H[c]	1.50	0.047

Bond Stretching Parameters

bond	l_0, Å	k, mdyn Å^{-2}	dipole moment
C≡C	1.212	15.6	0
≡C—C—	1.466	5.2	0.75
≡C—H	1.09	5.9	0

Angle Bending Parameters

angle	θ_0	k, mdyn rad^{-2}
—C≡C—H	180	0.36
—C≡C—C—	180	0.45
≡C—C—H	109.4	0.36
≡C—C—C—	109.5	0.45

Torsional Effect

	V_1	V_2	V_3
C—C—C—C≡	0.200	—0.260	0.093
H—C—C—C≡	0	0	0.400

Heat of Formation Parameters (kcal mol^{-1})

	C≡C	≡C—C	≡C—H
normal	59.015	−1.811	−3.205
strainless[d]	58.678	−1.459	−3.125

[a] For use with the 1977 force field (MM2). For alkane parameters, functions, etc., see ref 26. [b] These are the same as for olefinic carbon. [c] These are the same as for alkane and alkene hydrogen. [d] Strain is defined as $E + \Delta H$ (bonds) $- \Delta H$ (bonds, "strainless"), and parameters are chosen such that acetylene and propyne have zero strain. The number obtained directly might be called "inherent strain". To obtain from this number the ordinary strain energy, the excess torsional energy and conformational energy are added, as appropriate.[25]

the sequence of higher homologous 2-alkynes, 0.0, 0.09, 0.30, 0.52, etc., for the 2-alkynes. Analogous reasoning gives the numbers indicated in the tables for the 3-alkynes. Once we reach this point, we have to separately consider the two ends of the chain. So, for example, in 4-octyne, each end of the chain behaves in a manner analogous to 1-pentyne. Thus there are four ways to form a gauche conformation (compared with one for the anti) and there are also four ways to form a double gauche conformation. The calculated value for POP works out to be 0.18 kcal/mol. The other 4- and 5-alkynes were similarly examined and the Boltzmann distribution applied to give the numbers in Table I. This simple conformational mixing effect, apart from all other considerations, tends to make the enthalpy of the triple bond more negative the nearer the center of the molecule it is located. The effect is not very great, once the molecule becomes as large as C_{10}. The difference between the 3 and 4 positions is rather small, and between 4 and 5 quite negligible. Nonetheless, the trend is predicted to occur in a systematic manner which is similar to what is observed experimentally. We can also predict that the "end effect" has for practical purposes been reached in 5-decyne.

It turns out from the calculations that the population increment is essentially the only thing which affects the enthalpy as a function of the position of the triple bond, after it has reached position 3. This effect concerning the position of the triple bond is calculated to be rather small, as observed.

References and Notes

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