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Enthalpies of Hydrogenation of Phenylalkynes: Indirect Determination of the Enthalpy of Formation of Diphenylcyclopropenone

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This paper gives the enthalpies of hydrogenation of some phenylalkynes, measured in hexane solution, which lead to their enthalpies of formation. Measured enthalpies of hydrogenation of phenylacetylene, 1-phenyl-1-propyne, 1-phenyl-1-butyne, 1-phenyl-1-hexyne, diphenylacetylene, and diphenylbutadiyne are −66.1 ± 0.4, −62.2 ± 0.5, −62.7 ± 0.2, −62.6 ± 0.3, −59.6 ± 0.6, and −118.5 ± 1.0 kcal mol^{-1}, respectively. Our experimental result for diphenylacetylene is not in agreement with group additivity calculations and, when combined with a recent value for the decarbonylation of 2,3-diphenylcycloprop-2-en-1-one, leads to a resonance stabilization for that compound of 22 kcal mol^{-1}, or about twice the estimate obtained by the group additivity method.

By far the most frequently used method of determining enthalpies of formation ΔH_f of organic compounds is combustion calorimetry.[1] Enthalpies of formation of acetylenic compounds determined by this method are, however, not widely available in the literature.

Acetylenes add hydrogen rapidly and quantitatively under mild catalytic conditions, and, if the enthalpy of formation of the saturated reaction product is available, as it often is, the enthalpy of formation of the acetylene follows by Hess's law.

There are some advantages to determining ΔH_f of alkenes and alkynes by hydrogen calorimetry. Accordingly, we have measured the enthalpies of hydrogenation ΔH_h of several phenylalkynes and calculated the corresponding ΔH_f values with the objective of obtaining quantitative information on the energetic influence of the phenyl group on acetylene, some alkylacetylenes, and butadiyne. We present these results along with a critical comparison to the extant literature values.

In addition, our experimental value for the enthalpy of hydrogenation of diphenylacetylene (DPA), and the resulting enthalpy of formation, casts new light on the aromaticity of 2,3-diphenylcycloprop-2-en-1-one (DPCP) and, by analogy, the aromaticity of cyclopropene.

Theory

The enthalpy of hydrogenation of an alkyne is a quantitative measure of the difference in enthalpy between the alkyne and its product alkane. Because the heat of hydrogenation is always exothermic, the alkyne always has an enthalpy of formation that is more positive than the alkane. Because ΔH_h is small compared to heats of combustion, this difference can be measured with considerable absolute accuracy by hydrogen calorimetry, even though the relative precision of these experiments has never been competitive with combustion calorimetry.

There are some other reasons for determining ΔH_f values of alkynes by hydrogen calorimetry rather than by combustion calorimetry. Generally speaking, individual calorimetric results are difficult to obtain and difficult to evaluate once obtained. Enthalpies of formation of the alkanes have been obtained through a major research effort over many years that has generated many data which permit cross-checking to single out an erroneous result should one appear. Moreover, the method of molecular mechanics (MM) permits calculations to be carried out[2] that are the result of a composite force field incorporating many experimental results. This allows predictions to be made for new experiments that may differ in detail from the correct findings but will not suffer the catastrophe that can occur when a serious systematic error enters into a relatively small set of experimental calorimetric measurements. In short, if the MM calculations differ markedly from the experimentally determined enthalpy of formation of an alkane, the experiment had better be rechecked; the experimentalist has probably been prevented from publishing an error by the MM safety net.

This is not necessarily true of alkenes and even less true of alkynes because of the paucity of data on these two classes of compounds. An erroneous ΔH_f for one of these compounds looks pretty much like an accurate one.

Enthalpies of hydrogenation, however, tend to fall into distinct classes, making their comparison and evaluation easier. Generally, an enthalpy of hydrogenation that is seriously in error looks seriously in error. A case in point involves the combustion studies of norbornene and norbornane[3] that assigned to these compounds entirely plausible ΔH_f values of +15.1 and −12.0 kcal mol^{-1}, respectively. It is only after taking the difference between these two numbers, $\Delta H_h = -27.1$ kcal mol^{-1}, that they begin to look wrong. The hydrogen thermochemical literature shows that the unstrained cyclic double bond in cyclohexene has $\Delta H_h = -28.6$ kcal mol^{-1} in the gaseous phase.[4] This enthalpy change should be made larger in magnitude (more negative) by the relaxation of strain that occurs when a rigid double bond is hydrogenated to a single bond,[5] as in the norbornene–norbornane transformation. Instead, the value of 15.1 for ΔH_f of norbornene leads to a smaller value than the strainless enthalpy change; hence, it is suspect. Further study[6] showed that ΔH_h of norbornene is in fact −33.8 kcal mol^{-1}, which yields 21.8 kcal mol^{-1} for its enthalpy of formation.

A further reason to prefer hydrogen calorimetry for study of the thermochemistry of the higher alkynes is that

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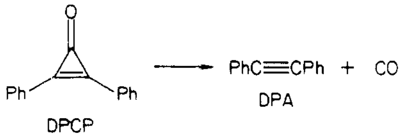
some diacetylenes and polyacetylenes may detonate under investigation by combustion calorimetry.[7a]

Aside from its intrinsic thermodynamic significance, the enthalpy of formation of DPA is interesting because it can be used to calculate the heat of formation of DPCP from the photoacoustic calorimetric determination[8] of the enthalpy of the reaction



(1)

There has been considerable recent interest in the resonance energy of DPCP[8,9] which follows directly from the enthalpies of formation of the products of reaction 1 in combination with its measured heat of reaction. Substantial resonance stabilization would be a weighty argument in favor of aromaticity of the molecule and, by implication, its simpler analogue, cyclopropenone.[9,10] Unfortunately, the experimental enthalpy of formation of DPA in the standard state was not known when these papers[8,9] were written, and resonance energy calculations were based on a bond-energy parameter,[9b] the reliability of which is not easy to judge.

The value[9] for ΔH_f of DPA that was used is 102.8 ± 1.0 kcal mol^{-1}, which, as noted previously, looks as good as any other until it is combined with the known and reliable[1,11] ΔH_f of diphenylethane (DPE), its hydrogenation product, which is 32.4 ± 0.3 kcal mol^{-1}. These enthalpies have a difference of 70.4 kcal mol^{-1} within rather small uncertainty limits; i.e., an acetylenic link stabilized on either end by phenyl groups is predicted to have a ΔH_h that is larger in magnitude than propyne.[12] At this point, something begins to look wrong.

Accordingly, we combined our value for ΔH_h of DPA with the ΔH_h of the hydrogenation product[1,11] (DPE) to arrive at an experimentally determined enthalpy of formation of DPA and to recalculate the resonance energy of interest, that of DPCP.

Results and Discussion

A single set of experiments of nine sequential runs of two hydrogenations each, one for the standard and one for the alkyne, is represented by each of the 12 entries above the horizontal lines in the center column of Table I. Each entry under the line in the center column corresponds to the grand mean of 18 paired measurements, 36 hydrogenations in all. The uncertainty of each single entry expresses 95% confidence limits on the experimental scatter of the calorimetric measurements. Uncertainty due to sample impurities is not included in these scatter limits. Uncertainties of the grand means are arithmetic means of the 95% C. L. values for the individual means, and the uncertainties of the ΔH_f values are the geometric means of the uncertainties of the ΔH_h values just described and the ΔH_f values of the reaction products taken from the literature sources given below.

Table I. Enthalpies of Hydrogen and Formation of Some Phenylalkynes

compd	ΔH_h, kcal mol^{-1}	ΔH_f, kcal mol^{-1}	lit. ΔH_h, kcal mol^{-1}
phenylacetylene	−65.92 ± 0.27		
	−66.17 ± 0.45		−70.7[7]
	−66.12 ± 0.06		−64.7[13]
		73.27 ± 0.41	
1-phenyl-1-propyne	−62.29 ± 0.56		
	−62.11 ± 0.39		
	−62.20 ± 0.48		
		64.09 ± 0.52	
1-phenyl-1-butyne	−62.93 ± 0.19		
	−62.47 ± 0.14		
	−62.70 ± 0.16		
		59.42 ± 0.25	
1-phenyl-1-hexyne	−62.32 ± 0.24		
	−62.77 ± 0.35		
	−62.55 ± 0.30		
		(54.0)[a]	
diphenylacetylene	−59.54 ± 0.59		−64.1[7]
	−59.73 ± 0.54		
	−59.64 ± 0.56		
		92.0 ± 0.64	
diphenylbutadiyne	−118.46 ± 0.87		
	−118.52 ± 1.10		
	−118.49 ± 0.99[b]		

[a] Approximate value. [b] Insufficient sublimation data for ΔH_f calculation.

Phenylacetylene. Flitcroft and Skinner determined ΔH_h for phenylacetylene to be −70.1 kcal mol^{-1} using ethanol as the calorimeter fluid. Appropriate correction for the enthalpy of solution of ethylbenzene in ethanol leads to −70.7 ± 1.0 kcal mol^{-1} for the pure liquid-to-liquid hydrogenation.[1,7b] Enthalpies of vaporization for the product and reactant are not available for calculation of the vapor-phase enthalpy of hydrogenation, but it seems unlikely that the vaporization enthalpies would differ by an amount sufficient to explain the discrepancy between the older values and the result reported here. It is more likely that a catalyst interaction (see below) is included in the earlier values, making them more exothermic than they should be by about 5 kcal mol^{-1}.

An earlier ΔH_h from our laboratory[13] is included in the rightmost column of Table I. It was measured with use of cyclohexane as the calorimeter fluid and, because of the negligible solvent interactions, is thought to be within experimental uncertainty of the vapor-phase value.[14] Our earlier value is within combined experimental uncertainties of the one we present here, but the new value should supersede it for reasons of improved experimental technique and apparatus.

Even if solvent interactions are not negligible, if the gaseous product and reactant of the hydrogenation interact with the solvent in the same degree (thermodynamically), the enthalpy of transfer from dilute solution to vapor phase is the same for reactant and product. For equal enthalpies of transfer, ΔH_h is the same in solution as it is in the vapor phase. We believe[14] that this condition is met to well within the 0.5 kcal mol^{-1} uncertainty limits arising from other sources.

Use of ΔH_f = 7.15 ± 0.19 kcal mol^{-1} for ethylbenzene obtained in the combustion studies of Rossini's group[15]

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leads to the enthalpy of formation for phenylacetylene in Table I. The resonance-stabilized benzene ring is not hydrogenated under the conditions described here, as indicated by GLC studies of the calorimeter fluid after a series of hydrogenations had been made. Despite sensitivity at the part per thousand level[16] for detection of stray peaks, GLC did not yield peaks other than those of the solvent and expected hydrogenation products of the standard and sample.

1-Phenyl-1-propyne. Combination with the combustion result of Rossini's group[1,15] of 1.89 ± 0.19 kcal mol^{-1} for *n*-propylbenzene yields the enthalpy of formation listed in Table I.

1-Phenyl-1-butyne. Combination with the result by Rossini's group[1,15] of −3.28 ± 0.19 kcal mol^{-1} for *n*-butylbenzene yields the value in Table I.

1-Phenyl-1-hexyne. No combustion value for the ΔH_f of *n*-hexylbenzene is available. Extrapolation from the previous three values yields −8.5 kcal mol^{-1} as a plausible estimate. Combination of this value with ΔH_h yields the result in Table I, also an estimate.

Diphenylacetylene. The enthalpy of formation of gaseous diphenylethane in the standard state has been determined, using bomb calorimetry, by several groups,[1,11,17] with excellent agreement. The most recent of these determinations[1,11] is also the selected value,[1] which leads to $\Delta H_f^\circ(g) = 32.4 \pm 0.3$ kcal mol^{-1}. Combining this with our enthalpy of hydrogenation yields $\Delta H_f^\circ(g) = 92.0 \pm 0.64$ kcal mol^{-1} for DPA, in serious disagreement with group additivity predictions. Use of our experimental value along with −9.9 ± 2.9 kcal mol^{-1} for the enthalpy of photodissociation of DPCP to DPA and CO and −26.42 ± 0.04 kcal mol^{-1} for the enthalpy of formation[1,18] of CO yields a heat of formation for DPCP of 75.5 ± 4 kcal mol^{-1}, lower by 10 ± 1 kcal mol^{-1} than the value calculated[8] with group additivities for DPA. This value is 21.7 kcal mol^{-1} lower than Greenberg's resonance-free model,[9] indicating strong stabilization, relative to that model, at least. The present value is in reasonably good agreement with the Hartree–Fock calculation cited by Greenberg[9] but not with the preliminary combustion calorimetric results of 87 kcal mol^{-1} cited there.

While these data were being prepared for publication, we received word of further combustion studies on DPCP reported by Greenberg, Liebman, and colleagues at the Bartlesville Energy Technology Center.[19] They found $\Delta H_f(g) = 75.93 \pm 2.0$ kcal mol^{-1} for DPCP. Assuming a ring strain[9] of 67 kcal mol^{-1}, these data yield a resonance energy of 21 kcal mol^{-1} in agreement with the results obtained by hydrogen calorimetry.

An unpublished enthalpy of sublimation of DPA[20] cited by Greenberg and Liebman can be combined with the enthalpy of formation of crystalline DPA measured by Coops et al.[1,21] and the enthalpies above to give 79.64 ± 4.1 kcal mol^{-1} for DPCP, which is within combined experimental error of the value derived from hydrogen calorimetry.

Table II. Stabilization Enthalpies of Some Methyl- and Phenylalkynes[a]

alkyne	methyl stabilization	phenyl stabilization
acetylene	methylacetylene	phenylacetylene
−74.6	−69.2 (5.4)	−66.1 (8.5)
1-propyne	2-butyne	1-phenyl-1-propyne
−69.2	−65.6 (3.6)	−62.2 (7.0)
1-butyne	2-pentyne	1-phenyl-1-butyne
−69.8	−65.6 (4.2)	−62.7 (7.1)
1-hexyne	2-heptyne	1-phenyl-1-hexyne
−69.2	−65.1 (4.1)	−62.6 (6.6)
phenylacetylene	1-phenyl-1-propyne	diphenylacetylene
−66.1	−62.2 (3.9)	−59.6 (6.5)

[a] Negative numbers are enthalpies of hydrogenation in kcal mol^{-1}. Positive numbers in parentheses are stabilization enthalpies relative to the compound listed in the leftmost column.

Diphenylbutadiyne. Enthalpies of combustion obtained by Coops et al.[1,21] on this substituted butadiyne and its hydrogenation product in the crystalline state are not comparable to the present results because the appropriate enthalpies of sublimation are not presently known.

Stabilization Enthalpies. Stabilization by the phenyl group is substantial in all cases as expected. One may conclude, from Table II, that "typical" phenyl stabilization of a triple bond is about 7 kcal mol^{-1} while that of a methyl group is only 3 kcal mol^{-1} less. One is impressed by the relative stabilizing power of the methyl group.

Table II shows that stabilization by both methyl and phenyl is about 20% larger for the first member of the series (stabilization relative to ethyne). This is analogous to the large stabilization of ethylene by one methyl group (propene relative to ethene) but not, incidentally, analogous to some of our preliminary findings on styrene.

When two stabilizing groups operate on the same bond, there is some attenuation in stabilizing power of the second substituent relative to the first; e.g., stabilization of phenylethyne by a second phenyl group is somewhat less than the "typical" value. This is analogous to the slight reduction in stabilization enthalpy conferred by the second methyl subsititution in *trans*-2-butene relative to 1-propene as compared to the stabilization of 1-propene relative to ethene.

Twice the ΔH_h for 1-butyne is −139.6 kcal mol^{-1}, which is almost exactly reproduced by Skinner's value of −139.4 kcal mol^{-1} for 1,5-hexadiyne with two isolated terminal triple bonds.[7] Butadiyne has not been studied, but conjugative stabilization of 5,7-dodecadiyne relative to 3,9-dodecadiyne is 3.9 kcal mol^{-1}. Summing the "typical" stabilization enthalpies attendant upon replacement of two terminal acetylenic hydrogens with phenyl groups and internal triple bond conjugative stabilization, one arrives at 2(7) + 3.9 = 17.9 kcal mol^{-1} as a predicted aggregate stabilization in diphenylbutadiyne. Adding this to $H_h = -139.6$ kcal mol^{-1} yields −121.7 kcal mol^{-1}, the predicted ΔH_h of diphenylbutadiyne, as contrasted to the measured value of $H_h = -118.5$ kcal mol^{-1}. It is likely that 3.9 kcal mol^{-1} is too low an estimate for the stabilization enthalpy of two conjugated triple bonds in this molecule.

Blank Measurements. Preliminary determinations of ΔH_h were more exothermic than anticipated; for example, 1-phenyl-1-hexyne yielded a value of −65.4 ± 0.4 kcal mol^{-1}, statistically identical with our previous value of −65.6 ± 0.4 kcal mol^{-1} for 2-hexyne.[14] It did not seem reasonable that the phenyl group should impart no more stabilization to the triple bond than a methyl group and, indeed, there was a trend shown toward lower values of ΔH_h as successive injections were made into the calorimeter. We have seen similar behavior in experiments on compounds containing an electronegative atom, such as the unsaturated

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ethers.[22] We speculate that the π-electron cloud of the phenyl group associates with the catalyst or its activated charcoal support in an exothermic way to cause an apparent ΔH_h that is too large in magnitude by the amount of the heat of association.

To test this hypothesis, we ran "blanks", described in the Experimental Section, designed to detect heat effects other than those due to hydrogenation. These led to an enthalpy change of -0.63 J for injection of 65 μmol of phenylacetylene into the system in the absence of hydrogen. The spurious heat effect is 9.6 kJ mol^{-1} or 2.3 kcal per mol of phenylacetylene but monotonically approaches zero after six to eight injections. A similar experiment was run on DPE with similar results. Subtracting the measured association blank from the ΔH_h referred to above yields $-65.4 - (-2.3) = -63.1$ kcal mol^{-1}, which is within the combined experimental uncertainties of the grand mean listed in Table I. These results are semiquantitative because neither the amount of Pd–C catalyst nor its homogeneity was precisely known. Nevertheless, the direction and approximate magnitude of the heat effect favors some kind of association mechanism involving the phenyl group and the catalyst or its support. Results for reactant and product are indistinguishable at this level of accuracy.

Experimental Section

Reagents. Alkynes and allylbenzene were obtained from Wiley Organics and certified to be 99% pure or better by the manufacturer. This was verified by GLC. The monophenylalkynes were slightly yellow. Color was removed by distillation at reduced pressure. GLC revealed no measurable impurities in the distillate. Other reagent sources have been given.[14]

Procedure. The method of hydrogen calorimetry has been described.[14] These studies differed from our published work on linear alkynes[14] only in that the calorimetric standard was allylbenzene rather than hexene. This change was made to minimize the difference in reaction medium interactions for the reactant and for the standard and because the kinetics of hexene hydrogenation were progressively slowed by the presence of accumulated aromatic product in the calorimeter. This kinetic effect did not occur when allylbenzene was used as the thermochemical standard.

A 10% w/w standard solution of allylbenzene in hexane was injected into a 25-mL solution calorimeter, at 2 atm of pressure of H_2, containing a slurry of Pd catalyst on carbon support in an inert solvent (hexane) and being stirred magnetically. Following this injection, a 10% solution of alkyne in hexane solvent was injected into the same calorimeter, and the thermal response was compared for the two hydrogenation reactions. Taking the enthalpy of hydrogenation of a terminal, unconjugated double bond[14b] to be -30.25 kcal mol^{-1}, one can calculate ΔH_h of the alkyne from the ratio of the heats produced. After the first few runs were discarded data were collected. The enthalpy of hydrogenation approximates the standard state value if, as we suppose,[14a] the conditions given in the Discussion section are fulfilled.

After a series of experiments, the calorimeter fluid was subjected to GLC analysis using a 30-m SE 30 capillary column. No peaks that would indicate incomplete reaction or side reactions were found except as indicated in the attempt to measure ΔH_h for DPCP. Numerous experiments[16] have been carried out on samples of calorimeter fluid that were intentionally contaminated with reactant or an anticipated side product. These experiments lead us to believe that capillary GLC is sensitive to undesired products present at one part per thousand or less.

Attempts to measure the enthalpy of hydrogenation of DPCP directly were unsuccessful. Thermal response was slow, and no unequivocal ΔT could be obtained. GLC and MS analysis of the calorimeter fluid showed several reaction products. Under the conditions that we use, DPA is, however, quantitatively and rapidly hydrogenated to DPE.

Blank Runs. A calorimeter was prepared that is identical with the one used in the main set of experiments except that it is electrically calibrated. Injections of a solution of DPA in hexane were made into the new calorimeter containing hexane and a normal catalyst charge but no hydrogen. This was followed by injection of pure hexane as a thermal blank to correct for a small temperature mismatch between the injected solution and the calorimeter fluid. Subtraction of the thermal blank from the heat effect of the first injection yielded the heat effect due to DPA in the absence of hydrogen. This was compared with the recorder deflection for an electrical calibration pulse of 1.0 J, and the ratio yielded the magnitude of the heat effect. A similar experiment was run on DPE, the hydrogenation product.

Acknowledgment. We acknowledge support from the NIH Minority Access to Research Careers program, the Research Corporation, through a Cottrell College Science Grant, and Long Island University for released time. We thank Raymond R. Mandra for obtaining and interpreting GLC–MS data on DPCP and its hydrogenation products.

Registry No. Phenylacetylene, 536-74-3; 1-phenyl-1-propyne, 673-32-5; 1-phenyl-1-butyne, 622-76-4; 1-phenyl-1-hexyne, 1129-65-3; diphenylbutadiyne, 886-66-8; diphenylacetylene, 501-65-5.

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Effects of 16-Heterosubstitution on the Regiochemistry of the *D*-Homo Rearrangement[1a]

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The 16β-phenylthio-, 16β-phenylseleno-, and 16β-dimethylphenylsilyl-substituted 3β,17α-dihydroxy-5-pregnen-20-ones have been prepared by nucleophilic ring opening of 16α,17α-epoxysteroids in order to study the influence of the 16-substituent on the regiochemistry of the *D*-homo rearrangement. It was found that the phenylthio substituent redirected the course of the base-catalyzed ketol rearrangement, resulting in quantitative formation of the usually unobserved 17β-hydroxy-17a-keto-17α-methyl-*D*-homo isomer, whereas phenylseleno or dimethylphenylsilyl substituents showed no influence. Thus, only S, but not Se or Si, seems capable of effectively stabilizing the negative charge in the α position in the transition state. On Lewis acid catalysis, however, neither S nor Se nor surprisingly Si had any effect on the regiochemistry of the rearrangements, resulting in the "normal" 17α-hydroxy-17a-keto-17β-methyl-*D*-homo isomers.

The α-ketol rearrangement of 17-hydroxy-20-keto-steroids, termed the *D*-homo rearrangement, was discovered in 1938[2] and has been the subject of investigation ever since.[3] Thus treatment of 17α-hydroxy-20-keto steroids

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