Heats of Formation of C_4H_6 Hydrocarbons[1]

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Abstract: The heats of formation of 1-methylcyclopropene, methylenecyclopropane, cyclobutene, and bicyclobutane have been determined *via* flame calorimetry. The effect of bond angle deformation on heats of formation is discussed.

A detailed interpretation of the thermal and solvolytic reactions of cyclic compounds requires a knowledge of the heats of formation of the reactants and products. Although much data are available concerning acyclic compounds and benzene derivatives, relatively little is known about the thermochemistry of cyclic compounds. We now wish to report the first results of a program to obtain such data.

The cyclic C_4H_6 hydrocarbons are of considerable interest since they incorporate trigonal centers into cyclopropane and cyclobutane rings, and since bicyclobutane is the most strained of the bicyclic hydrocarbons. 1-Methylcyclopropene,[3] methylenecyclopropane,[4] cyclobutene,[5] and bicyclobutane[6] were prepared by standard methods. Each of the hydrocarbons was purified by preparative vapor phase chromatography, using conditions which would permit ready separation from the isomeric hydrocarbons. The purity was checked by examining the nmr spectra of neat samples under conditions which gave large C^{13} satellite peaks. No peaks due to other compounds could be seen above the normal noise level. It was estimated that 0.2% of any of the isomeric compounds could easily be seen, and that 0.1% could probably be seen. Similarly, reinjection of the purified sample onto an analytical vpc column gave no detectable peaks due to impurities.

The heats of combustion were determined by flame calorimetry, using a calorimeter similar to that which we previously used for cyclopropene.[7] The heat evolved in the combustion was determined *via* an electrical calibration immediately following each calorimetric run. As a check on the apparatus and the procedure, the heat of combustion of propylene was determined giving the data in Table I. Both the precision and the agreement with the previous work were quite satisfactory.

Table I. Heat of Combustion of Propylene at 25°

Run no.	$-\Delta H_c°$, kcal/mol	Average	Previous value[a]
1	491.83		
2	492.17	491.83 ± 0.27	491.82 ± 0.15
3	491.50		

[a] F. D. Rossini and J. W. Knowlton, *J. Res. Natl. Bur. Std.*, **46**, 106 (1937).

The heats of combustion of the four hydrocarbons were determined in the same manner giving the results summarized in Table II. Finally, the heats of formation derived from these quantities are compared with the previous values for the acyclic C_4H_6 isomers in Table III.

Table II. Heats of Combustions of C_4H_6 Isomers at 25°

Compound	Run no.	$-\Delta H_c°$, kcal/mol	Average
Cyclobutene	1	618.09	618.60 ± 0.36
	2	618.88	
	3	618.84	
Methylenecyclopropane	1	629.32	629.07 ± 0.43
	2	629.43	
	3	628.46	
1-Methylcyclopropene	1	639.44	639.36 ± 0.27
	2	639.00	
	3	639.65	
Bicyclobutane	1	632.86	633.05 ± 0.19
	2	633.23	

Table III. Heats of Combustion and Formation of C_4H_6 Isomers at 25°

Compound	$-\Delta H_c°$, kcal/mol	ΔH_f, kcal/mol	Ref
1,3-Butadiene	607.16 ± 0.18	+26.0 ± 0.2	*a,b*
2-Butyne	615.84 ± 0.23	+34.7 ± 0.2	*a*
Cyclobutene	618.60 ± 0.36	+37.5 ± 0.4	
1,2-Butadiene	619.93 ± 0.13	+38.8 ± 0.1	*a,b*
1-Butyne	620.04 ± 0.20	+39.5 ± 0.2	*a*
Methylenecyclopropane	629.07 ± 0.43	+48.0 ± 0.4	
Bicyclo[1.1.0]butane	633.05 ± 0.19	+51.9 ± 0.2	
1-Methylcyclopropene	639.36 ± 0.27	+58.2 ± 0.3	

[a] E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **19**, 249 (1937). [b] E. J. Prosen, F. W. Maron, and R. D. Rossini, *ibid.*, **42**, 269 (1949).

The data permit several interesting comparisons. First, the heats of hydrogenation of the cycloalkenes are

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(1) This work was supported by the Army Research Office, Durham.

(2) Taken from the Ph.D. Thesis of R. A. F., 1967.

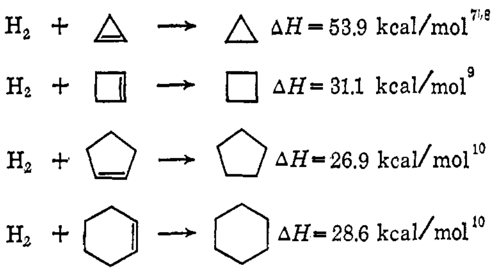
(3) F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).

(4) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Board, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

(5) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

(6) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters*, 2173 (1963); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

(7) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).

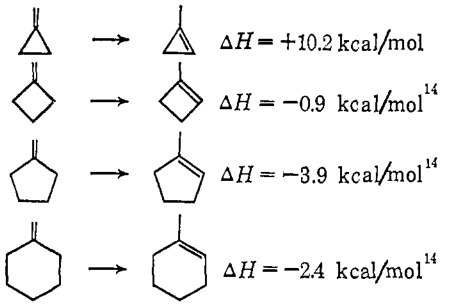


The difference between cyclopentene and cyclohexene has been attributed to the increase in torsional strain on going from cyclopentene to cyclopentane.[10] A similar factor is operative with cyclobutene. Taking the torsional barrier as approximately 3 kcal/mol, the torsional strain of cyclobutene is 3 kcal/mol. The torsional angles for cyclobutane are about 24°,[11] giving 1.95 kcal/mol as the torsional strain per methylene pair, or 7.7 kcal/mol for the molecule. Thus the torsional strain is increased by ~4.7 kcal/mol on hydrogenation.

Open-chain analogs are conventionally taken as models of unstrained systems. Thus, the Franklin group equivalents[12] are appropriate for calculating the energies of unstrained models. In this way, the strain energies of cyclobutene and cyclobutane were calculated to be 28.5 and 26.1 kcal/mol, respectively. Correcting for the torsional strain gives the angle strain as about 25.5 and 18.4 kcal/mol, respectively.[13] Thus, hydrogenation of cyclobutene to cyclobutane reduces the angle strain by about 7 kcal/mol.

The strain energies of cyclopropene and cyclopropane, again estimated using Franklin's group equivalents, are 52.6 and 27.5 kcal/mol, respectively. Correcting for the torsional strain of cyclopropane (about 9 kcal/mol) gives the angle strain as 52.6 and 18.5 kcal/mol, respectively. In this case, hydrogenation results in a decrease in angle strain of about 34 kcal/mol. Thus, whereas a modest change in angle strain is found in the hydrogenation of cyclobutene, a very large change is found in the hydrogenation of cyclopropene.

The effect of introducing only one trigonal center into each of these rings may be seen in a comparison of the heats of isomerization of exocyclic to endocyclic double bonds. The three-membered ring compounds represent the first case in which the exocyclic double bond is found to be more stable than the endocyclic double bond. Again, this is due to the difficulty in creating a second trigonal center in a cyclopropane ring.



The strain energies of cyclopropane, methylenecyclopropene, and 1-methylcyclopropene are 27.5, 41.0, and 53.1 kcal/mol, respectively, leading to an increase in total strain of about 13 kcal/mol per trigonal center. This may be contrasted with the four-membered ring compounds for which the increase in total strain per trigonal center is only about 1 kcal/mol. It is clear from these results that whereas the geometry of cyclopropane can be accommodated by bent bonds and the attendent extra bonding possibilities discussed by Coulson and Moffitt,[15] leading to strain energy not much different than that of cyclobutane, such is not readily possible when trigonal centers are introduced. If, as has been previously suggested,[16] the olefinic C–H bond in cyclopropene is formed using a carbon orbital approaching sp hybridization, the bonds to the methylene carbon would have very large p character, leading to a relatively weak C–C bond.

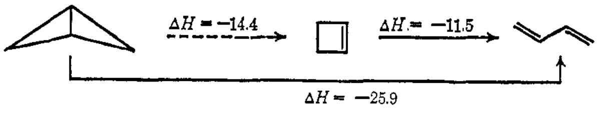
Having the heats of formation of 1-methylcyclopropene and of cyclopropene, it is possible to see whether or not hybridization at the olefinic carbon will affect the stabilization due to methyl substitution. Pertinent data are summarized in Table IV. It appears that the effect on cyclopropene is essentially the same as on unstrained alkenes, and that the variation in the effect is more a function of bond type than of hybridization.

Table IV. Effect of Methyl Substitution on Heats of Formation

Compound	ΔH_f, kcal/mol[a]	$\Delta\Delta H_f$, kcal/mol
Cyclopentane	−18.46	7.0
Methylcyclopentane	−25.50	
Cyclohexane	−29.43	7.6
Methylcyclohexane	−36.99	
cis-2-Butene	−1.67	8.5
2-Methyl-2-butene	−10.17	
cis-2-Pentene	−6.71	8.3
2-Methyl-2-pentene	−14.96	
Cyclopropene	66.9	8.4
1-Methylcyclopropene	58.2	
Acetylene	54.19	9.9
Propyne	44.32	9.4
2-Butyne	34.97	

[a] Except for cyclopropene and methylcyclopropene, the data are from the American Petroleum Institute tables.

Finally, the thermochemistry of the conversion of bicyclobutane to butadiene may be considered. Although the conversion of bicyclobutane to butadiene could involve cyclobutene as an intermediate, the direct conversion to butadiene is considerably more exothermic. Thus, except in unusual circumstances, cyclobutene is probably not an intermediate.[17]



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(8) F. D. Rossini and J. W. Knowlton, *J. Res. Natl. Bur. Std.*, **46**, 106 (1937).

(9) S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, 71, 261 (1952).

(10) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, 61, 1868 (1939).

(11) K. B. Wiberg and G. M. Lampman, *ibid.*, **88**, 4429 (1966).

(12) J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949).

(13) This estimation of angle strain assumes that the effects of nonbonded interactions will be about the same for both molecules. Our previous calculations[11] suggest that this may be a reasonable assumption.

(14) Based on the heats of hydrogenation in acetic acid solution at 25°: R. B. Turner, "Kekule Symposium," Butterworth and Co. Ltd., London, 1959, p 67; R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958).

(15) C. A. Coulson and W. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

(16) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

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Experimental Section

Calorimeter. The reaction vessel was constructed of glass using a design similar to that of Rossini.[18,19] It permitted a stream of the hydrocarbon, diluted with helium, to be premixed with oxygen prior to burning in an atmosphere of oxygen. The reaction vessel was immersed in water contained in a covered dewar flask which was equipped with a constant-speed stirrer, a thermistor probe, and a heater. The exit gases from the vessel passed through a spiral equilibrating tube also immersed in the calorimeter water. The water and carbon dioxide formed in the combustion were absorbed by Anhydrone and Ascarite, respectively. The water in the dewar was at 25.0° at the beginning of the combustion experiment, and the dewar was immersed in a water bath at 28.000 ± 0.005°.

Combustion. After a 16-min fore period, during which the temperature change was noted, the hydrocarbon mixture was passed into the calorimeter. At 20 min, the combustion was initiated by an electrical spark. The combustion was allowed to proceed until about a 2° temperature rise was noted. During this period, temperature readings were taken periodically, and this was continued until 44 min from the beginning of the experiment. The last 8 min was taken as the after period. The amount of water vapor formed was determined by weighing the Anhydrone tube; the latter was returned to the exit line, and the calorimeter was swept out with oxygen. The Ascarite tube was weighed after 0.5 hr, but the system was swept overnight in order to collect all of the water. The weights of water and carbon dioxide agreed within 0.7% of the theoretical ratio, and the weight of hydrocarbon used was based on the carbon dioxide since it should be the more accurate of the two.

The electrical calibration was performed immediately after each combustion experiment in order to minimize errors. The temperature data were collected in a fashion similar to that of the combustion, with a fore period, a heating period, and an after period. During the heating period, the voltage across and the current through the heater were determined using a precision potentiometer. The time of heating was determined using an electronic clock with a precision of better than 0.01%.

The heat equivalent of the calorimeter and the heat of combustion were determined using a computer program which calculated the stirring and conduction energies from the fore and after periods and corrected the combustion or heating periods by integrating the stirring and conduction energies over the period. Corrections were made for the spark energy, the heat of vaporization of the water which appeared as water vapor at the end of the combustion, and the heat capacity of the gases which flowed through the calorimeter.

Since the hydrocarbon entering the calorimeter was at the water bath temperature, 28°, a small correction was necessary to obtain the heat of combustion at 25°. This correction was calculated to be 0.1 kcal/mol, and the values in Tables I and II have been corrected in this way. The complete experimental data and detailed calculation are given in the thesis of R. A. F. which is available through University Microfilms.

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(18) F. D. Rossini, *J. Res. Natl. Bur. Std.*, 6, 1 (1931).

(19) The calorimeter is described in detail in the thesis of R. A. F., which is available from University Microfilms, Ann Arbor, Mich.

Factors Influencing the Rates of Reaction at Arylmethyl Carbon Atoms. An Evaluation of the Importance of Steric Effects within the SCF–LCAO Approach

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Abstract: The relationships obtained by correlating the relative rates of arylmethyl ion formation with the corresponding changes in calculated π energies have been reexamined. Inclusion of nonbonded interactions does not favorably affect the HMO results; however, in many cases the use of these interactions with the SCF results improves the precision of the correlation. For nonalternant molecules the change in angle strain upon reaction may also introduce a pronounced effect.

The Hückel molecular orbital (HMO) approach provides a satisfactory treatment for alternate hydrocarbons; however, because of neglect of electronic interactions, calculations on nonalternants, ions, and heterocycles often prove less reliable.[1] For these latter systems the use of some self-consistent field (SCF) method can usually ameliorate the results. A comparison of attempts to correlate the rates of formation of arylmethyl ions, (shown in eq 1 and 2) by the two treatments illustrates this variance.

$$\mathrm{ArCH_3 + B^- \longrightarrow ArCH_2^- + BH} \qquad (1)$$

$$\mathrm{ArCH_2X \longrightarrow ArCH_2^+ + X^-} \qquad (2)$$

Streitwieser and Langworthy have examined the rates of formation of arylmethyl anions.[2] Correlations with HMO calculations were successful only if the compounds were divided into two sets. One, noted as the phenyl or β′-naphthyl type, was considered to involve no essential change in steric factors upon undergoing reaction. The second class of molecules was composed of compounds similar to α-methylnaphthalene, where upon going to the transition state (here taken as being equivalent to the planar ion) severe nonbonded interactions might occur between a hydrogen atom on the exocyclic carbon atom and one in a *peri* site such as the 8 position in naphthalene. When this dichotomy was employed, a fair correlation of the data was obtained, although certain compounds showed an unexpectedly large deviation from the relationship. When the same experimental data were utilized in an SCF approach, however, a single excellent correlation was observed.[3]

This study was undertaken to test the question of whether the steric factor predicted by HMO results is truly present. The possibility of such *peri* interactions is intuitively attractive despite the fact that SCF results

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