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Ab Initio Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Cyclic C_5 Hydrocarbons

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We have obtained Δ_fH^{298} for 11 C_5 cyclic hydrocarbons by calculating $\Delta_{hyd}H^{298}$ and $\Delta_{isom}H^{298}$ *via* the G2(MP2) and G2(MP2,SVP) *ab initio* methods, taking Δ_fH^{298}(cyclopentene) as a known reference point. The arithmetic mean deviation between G2(MP2) calculated Δ_fH^{298} and experimental Δ_fH^{298} values is <1 kcal mol^{-1} for the 5 compounds that have been studied experimentally.

Recently,[1] we carried out G2 and G2(MP2) *ab initio* calculations on the enthalpies of hydrogenation ($\Delta_{hyd}H^{298}$) and isomerization ($\Delta_{isom}H^{298}$) of 20 reactions among a set of 10 C_4 unsaturated and saturated hydrocarbons including tetrahedrane, cyclobuta-1,3-diene, and methylenecyclopropene. Knowing the enthalpy of formation (Δ_fH^{298}) of any member of the set permits one to calculate Δ_fH^{298} of any other member of the set. The advantages of calculating Δ_fH^{298} this way are (1) the experimental heats of formation[2] of $C_{(g)}$ and $H_{(g)}$ do not appear explicitly in the calculation, (2) the "higher level correction" (HLC), a purely empirical correction in G2 and G2MP2 calculations, drops out, and (3) correction of the energy at 0 K (E_0) to $\Delta_{hyd}H^{298}$ is simplified in most cases and need not involve computation of heat capacities at constant pressure (C_p) for the several hydrocarbons. Comparison with experimental values of $\Delta_{hyd}H^{298}$, Δ_fH^{298} from combustion and hydrogenation calorimetry, and computed Δ_fH^{298} values obtained by the method of isodesmic or homodesmotic reactions[3] shows that the method is reliable to within 1 kcal mol^{-1} for the cyclic C_4 compounds studied.

We wish to address (3) questions in this paper. (1) Can the method be extended beyond the 19 C_2, C_3, and C_4 hydrocarbons already studied? (2) Will there be any decrease in accuracy of G2(MP2) results as larger molecules are studied? (3) Can the simplified G2(MP2,SVP) method[4] be used without substantial loss in reliability?

Computational Methods

Input files were created by drawing a starting geometry with the graphical user interface of PCMODEL V 6.0[5] followed by semiempirical optimization using the PM3 Hamiltonian of MOPAC 6.0.[6] The Gaussian input file was written into the .ARC file of MOPAC using the **aigout** keyword. The *ab initio* calculations described here were carried out using the program[7] Gaussian 94, Revision C.2. The more resource-intensive calculations were carried out at the Pittsburgh Supercomputing Center.

G2. G2 methods have been described.[8] Briefly, the G2 method is based on a calculation at the 6-311G(d,p) MP2 *ab initio* level to which a series of corrections are made, the magnitude of each correction being determined by calculations at both higher and lower basis set levels and at three levels of post-Hartree−Fock computations, MP2, MP4, and QCISD(T). The object is to approximate the molecular energy that one would have obtained at the QCISD(T)/6-311+G(3d,2p) level, which is not directly attainable, for other than the smallest molecules, using present-day computers.

The total energy of the molecule (ion or radical) at 0 K is obtained by adding the fully corrected G2 energy (E) to the zero-point energy (E(ZPE)) and an empirical correction (HLC)

$$E_0 = E + E(\text{ZPE}) + \text{HLC}$$

which leads to its energy of atomization and other molecular−energetic properties.[4]

The reliability of the G2 method has been confirmed,[8,9] but it is too demanding of CPU time and system memory to encourage excursions into energy calculations for molecules containing more than four or five non-hydrogen atoms. Consequently, simplified methods have been sought that are less demanding of computer resources but are still capable of producing thermochemical data that are reliable to within an arbitrarily selected limit of ±2 kcal mol^{-1}.

G2(MP2). In G2(MP2) theory,[10] basis set corrections are combined as a single correction $\Delta_{MP2} = E$[MP2/6-311+G(3df,2p)] − E[MP2/6-311G(d,p)] which is applied to E[QCISD(T)/6-311G(d,p)] to approximate the solution that would have been obtained at the QCISD(T)/6-311+G(3df,2p) level; that is, the assumption is made that the basis set correction Δ_{MP2} and the post-Hartree−Fock corrections from MP2 to QCISD(T) are additive. The advantage is that two CPU- and memory-intensive MP4 calculations are eliminated from the G2 procedure. Indications so far are that the sacrifice in accuracy is small.

G2(MP2,SVP). G2(MP2,SVP) is a relatively recent modification of the G2 procedure[4] in which the 6-311G(d,p) basis set is reduced to 6-31G(d) for the QCISD(T) calculation and for the composite correction Δ. Now, $\Delta_{MP2,SVP} = E$[MP2/6-311+G(3df,2p)] − E[MP2/6-31G(d)]. Other than these changes, made to conserve computer resources (and, thereby, to study larger molecules), the procedure is the same as G2(MP2).

Δ_fH^{298}. Once having E_0 for a set of saturated and unsaturated isomeric hydrocarbons and for H_2, $\Delta_{hyd}E_0$ and $\Delta_{isom}E_0$ follow for hydrogenations and isomerizations connecting the set. These are the same as $\Delta_{hyd}H$ and $\Delta_{isom}H$ at 0 K.

One of the advantages of calculating Δ_fH through $\Delta_{hyd}E_0$ and $\Delta_{isom}E_0$ from any of the G2 family of procedures is that the empirical "higher level correction" (HLC) drops out. The HLC is not small (5.0 mhartrees per shared pair of valence electrons in G2 theory). Alkenes, however, always have one shared pair fewer than alkanes, hence in the reaction

$$\text{alkene} + H_2 \rightarrow \text{alkane} \qquad (1)$$

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the extra pair is supplied by H_2 and HLC drops out of the calculation

$$\Delta_{\mathrm{hyd}}E_0 = E_0(\mathrm{alkane}) - [E_0(\mathrm{alkene}) + E_0(\mathrm{H_2})]$$

Nor do the *experimentally* determined heats of formation of $C_{(g)}$ and $H_{(g)}$ appear explicitly in the calculation of $\Delta_f H^{298}$ from $\Delta_{\mathrm{hyd}}H^{298}$ and $\Delta_{\mathrm{isom}}H^{298}$ as they do in the "atomization" procedure[2] for obtaining $\Delta_f H^{298}$. While implicit in $\Delta_f H^{298}$ of an alkene or alkane, the experimental error in determining $\Delta_f H^{298}$ of the molecule is encountered once, not as a multiple of the number of carbon and hydrogen atoms in the molecule.

The temperature correction from 0 to 298 K is obtained directly from the suite of calculations called up by the **g2mp2** keyword in the route section of a Gaussian input file. In G2-(MP2,SVP) calculations, in the absence of internal rotation, the temperature correction is simple and does not really require knowledge of C_p values for the hydrogenation reactants and products. C_p values, though they may vary widely among the compounds in any set of hydrocarbons, are not very different for any reactant−product pair, hence $C_p(\mathrm{alkane}) - C_p(\mathrm{alkene}) \cong 0$. Thus, $\Delta_{\mathrm{hyd}}C_p$ in reaction (1) is dominated by $C_p(\mathrm{H_2})$ and is approximately the same for all hydrogenations. In prior G2-(MP2) calculations, the mean correction has been shown to have an upper limit of −2.0 kcal mol^{-1} and an arithmetic mean for actual calculations of −1.9 kcal mol^{-1}. In isomerizations, $\Delta_{\mathrm{isom}}C_p$ for the reaction is regarded as negligible.

Replacement of a methylene group by a methyl group by either hydrogenation or isomerization brings about the loss of a vibrational mode and its replacement by an internal rotor. If the vibrational mode was inactive below 298 K and if the rotation is free, the heat capacity is increased by $R/2 = 0.99$ cal K^{-1} mol^{-1}. If, further, methyl rotation is activated about halfway between 0 and 298 K, the temperature correction of the hydrogenation or isomerization is increased by 0.15 kcal mol^{-1}. See ref 11 for discussion of a similar problem in toluene.

Results

Simple Huckel theory suggests that the ground state might be a triplet in some of the molecules in Table 1. Indeed, the **stable** keyword[12] applied to the 6-31G(d,p) singlet indicated **rhf → uhf** wave function instability for dimethylenecyclopropane, methylmethylenecyclopropene, and cyclopentadiene. Higher-level **uhf** investigations of the triplet state either failed to converge or gave an energy substantially higher than the singlet. Computer resources were soon exceeded in our attempts to investigate this question further. It is our present opinion that triplet states indicated at lower levels of computation are, owing to geometric distortion found by the higher level calculations, not the ground states, i.e., that the singlet is the ground state. In support of this, we cite agreement between $\Delta_f H$ values calculated for cyclopentadiene and those from experimental thermochemical measurements in Table 2.

Geometries. Details of the 6-31G(d) MP2 optimized geometries of all of the molecules in Scheme 1 are included in the Supporting Information. The structures being quite rigid, their geometries are simple and very close to what one would construct using ball-and-stick models. Only a few salient geometric features will be mentioned here.

The angle of the methylene and methyl groups away from the apices of an equilateral or nearly equilateral triangle differ little from the expected 150°. Methylene groups have their hydrogen atoms in the cyclopropyl plane, and 1,2-dimethylcyclopropene has a plane of symmetry bisecting the double bond, owing to 1,4 eclipsing of the methyl hydrogens. In 1,3-dimethylcyclopropene, the inter-methyl radial angle is 120.6°, and in *cis*-dimethylcyclopropane, there is again a mirror plane separating the eclipsed methyls with an inter-methyl radial angle of 121.5°.

TABLE 1: Enthalpies (in kcal mol^{-1}) of Hydrogenation and Isomerization of C_5 Hydrocarbons

	G2(MP2)		G2(MP2,SVP)		expt	Δ	
	0 K	298 K	0 K	298 K	298 K	exp − calc	
A	3.9	4.2	4.1	4.4			
B	−47.5	−48.4	−47.9	−48.8			
C	45.6	45.5	46.0	45.9			
D	−35.9	−37.6	−34.9	−36.6			
E	−25.1	−26.5	−24.0	−25.4			
F	−39.8	−41.8	−39.0	−41.0			
G	−29.0	−30.7	−28.0	−29.7			
H	−31.5	−33.1	−30.5	−32.1			
I	15.9	15.3	17.4	16.8			
J	−21.7	−23.5	−20.9	−22.7	−24.4 ± 0.3[a]	−0.9	−1.7
					−23.9 ± 0.4[b]	−0.4	−1.2
K	6.8	4.9	8.2	6.3			
L	−67.3	−69.0	−67.0	−68.7			
M	−38.8	−40.7	−37.8	−39.7			
N	10.8	11.1	10.9	11.2			
O	−2.5	−2.4	−2.5	−2.4			
P	−37.7	−38.8	−38.3	−39.4			
Q	28.5	28.3	29.2	29.0			
R	−37.8	−39.6	−36.9	−38.7			
S	−36.5	−38.3	−35.5	−37.3	−38.1 ± 0.1[c]		
					(−38.7 ± 0.4)[d]	−0.4	−1.4
T	−48.6	−50.7	−47.8	−49.9			
U	−47.3	−49.4	−46.5	−48.6			
V	−44.7	−47.0	−44.0	−46.3	−45.1 ± 1.0[c]		
					(−45.7 ± 1.4)[d]	1.3	0.6
W	−62.2	−65.0	−61.4	−64.2			
X	−24.6	−26.2	−23.4	−24.6	−27.0 ± 0.2[e]	−0.8	2.0
Y	−53.1	−54.6	−52.2	−53.7	−55.1 ± 0.4[f]	−0.5	1.4
					−56.1 ± 0.1[g]	−1.5	2.4
Z	1.3	1.3	1.3	1.3	1.5[h]	0.2	0.2
AA	−17.5	−18.0	−17.4	−17.9			

[a] Obtained by difference between the experimental value[15] for hydrogenation to cyclopentane and reaction X. [b] Obtained by difference between the experimental value[16] for hydrogenation to cyclopentane and reaction X. [c] From ref 17. [d] Corrected for enthalpy of solution; see text. [e] From ref 18. [f] From ref 17. [g] From ref 16. [h] From ref 19.

The cyclopentenes and cyclopentane are unexceptional, as are the bicyclopentyl compounds. The computed "flap angle" of cyclopentene is 22.3° (lit. value[13] 23.3 ± 1.0°). The angles at the fusion of the cyclopropane ring and the cyclobutene(ane) ring in bicyclo[2.1.0]pent-2-ene and bicyclo[2.1.0]pentane are 66.7° and 65.5°. We are not aware of experimental values for these angles.

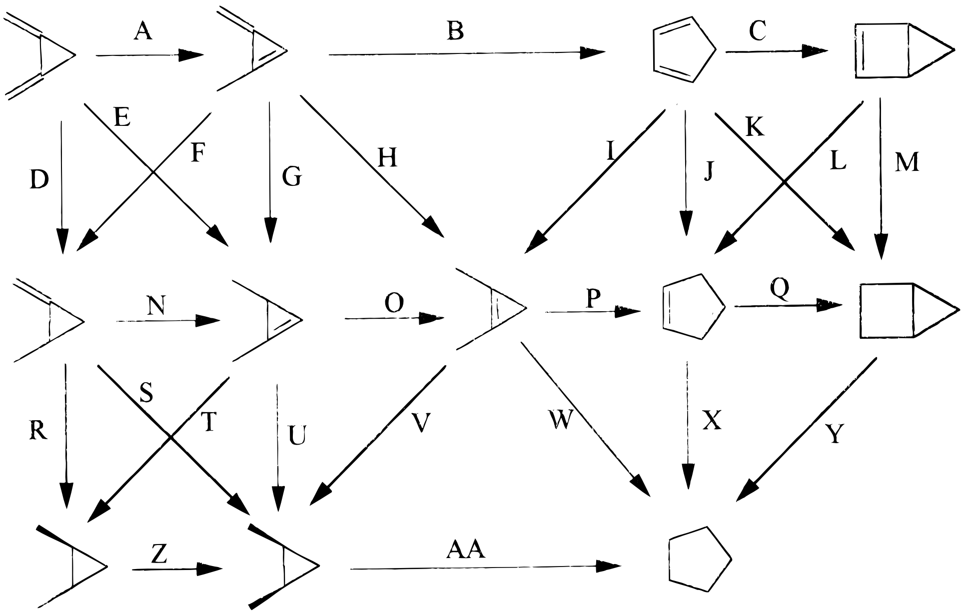
Energies. The G2(MP2) computed values of the total energy at 0 K, the G2(MP2) enthalpy at 298 K, and the G2(MP2,SVP) values of the energy at 0 K are given in Table A, (Supporting Information) for the 12 C_5 cyclic hydrocarbons in Scheme 1. Differences between G2(MP2) and G2(MP2,SVP) E_0 values have a regular pattern. Values of E_0 for the dienes and bicyclo-[2.1.0]pent-2-ene by G2(MP2) are 0.1 ± 0.3 mhartrees lower than E_0 by G2(MP2,SVP). Cyclopenta-1,3-diene has the largest deviation in this group (0.59 mhartrees). For monoenes, E_0 by G2(MP2) is 1.7 ± 0.4 mhartrees lower than it is by G2(MP2,SVP), and for the cycloalkanes, it is 3.4 ± 0.1 mhartrees lower. Numerous thermochemical cycles are evident in Scheme 1. They yield $\Delta_{\mathrm{cycle}}H^{298} = 0$ to within 0.1 kcal mol^{-1} rounding error.

Using these values and E_0 for hydrogen, we obtained ΔE_0 and ΔH^{298} for 27 hydrogenations and isomerizations designated by letters in Scheme 1. Table 1 gives results for seven simple hydrogenations, nine isomerizations, and 12 hydrogenations with concomitant isomerizations. G2(MP2) values of ΔH^{298} are

TABLE 2: $\Delta_f H^{298}$ (in kcal mol^{-1}) from G2(MP2) and G2(MP2,SVP) *ab Initio* Calculations and from Experimental Measurements

	G2(MP2)	G2(MP2,SVP)	expt	Δ exp − calc	
hydrogen	0	0	0		
dimethylenecyclopropane	75.8	75.2			
methylenemethylcyclopropene	80.0	79.6			
methylenemethylcyclopropane	38.2	38.7			
1,2-dimethylcyclopropene	46.9	47.5			
1,3-dimethylcyclopropene	49.4	49.9			
cis-dimethylcyclopropane	−0.1	1.3	−0.3 ± 0.4	−0.2	−1.6
trans-dimethylcyclopropane	−1.4	−0.2	−1.3 ± 0.4	0.1	−1.1
1,3-cyclopentadiene	31.6	30.8	32.5 ± 0.3	0.9	1.7
			32.0 ± 0.4	0.4	1.2
cyclopentene[a]	8.10	8.10	8.10 ± 0.3		
cyclopentane	−18.1	−16.5	−18.3 ± 0.2	−0.2	−1.8
bicyclopentene	77.1	76.8			
bicyclopentane	36.4	37.3	36.8 ± 0.5	0.4	−0.5
			37.8 ± 0.3	1.4	0.5
			arithmetic mean unsigned deviation	0.5	1.1
			arithmetic mean signed deviation	0.4	−0.2

SCHEME 1

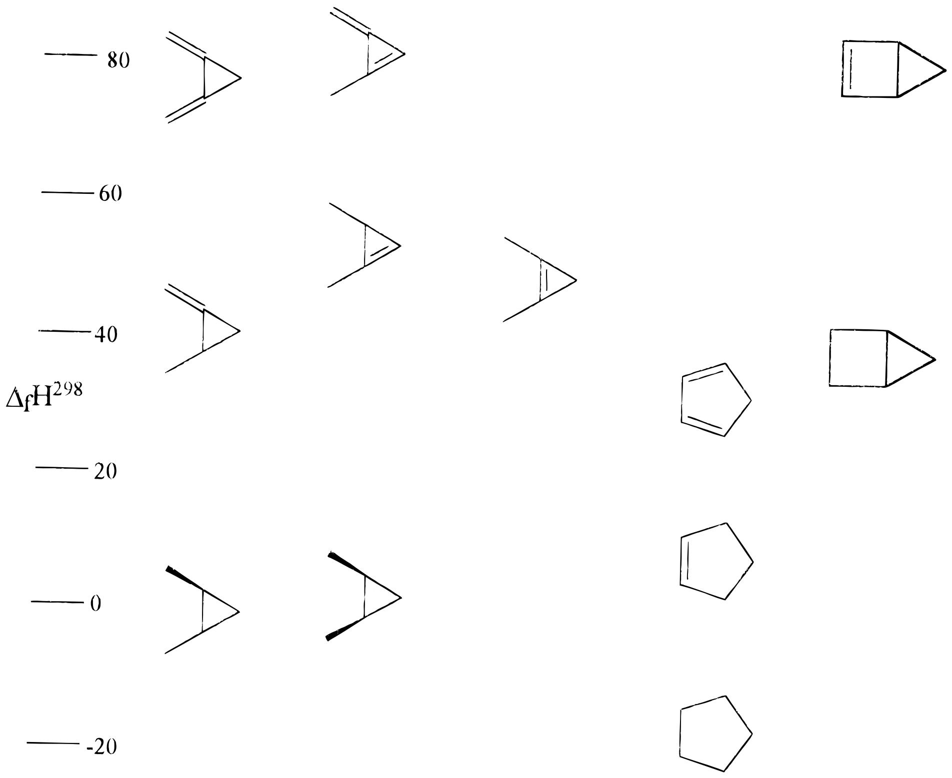


given in column 2 of Table 1. The correction from ΔE_0 to $\Delta_{hyd}H^{298}$, which is given by the G2(MP2) procedure, was taken from columns 1 and 2 in Table 1 and applied to G2(MP2,SVP) results in column 3 to obtain column 4. Correction of $\Delta_{hyd}H^0$ to $\Delta_{hyd}H^{298}$ has an arithmetic mean of −1.8 ± 0.2 kcal mol^{-1} within a range of 0.3 kcal mol^{-1}. This is in comparison with −1.9 ± 0.2 for the C_2, C_3, and C_4 hydrocarbons described earlier in this series.[1] Experimental values of $\Delta_{hyd}H^{298}$, and one $\Delta_{isom}H^{298}$ are given in column 5 of Table 1. Where two values are given (reactions J and Y), independent measurements were made by different research groups. Values in parentheses have been corrected by 0.6 kcal mol^{-1}, which is our estimate of the solvent effect to be expected in carrying out hydrogenations of an alkene or cycloalkene in glacial acetic acid.[14] We believe that this correction adds about 0.3 kcal mol^{-1} to the uncertainty of the experimental measurement. The experimental value of $\Delta_{hyd}H^{298}$ of bicyclopentane to cyclopentane in Table 1 is not corrected for solvent effects on the grounds that it is an alkane–alkane transformation, not a normal hydrogenation. We believe that solvent effects associated with hydrogenations of, e.g., cycloalkenes in glacial acetic acid, are due to association of the polar solvent with the π electrons of the double bond.

Comparison with Experiment. Hydrogenation of both methylmethylenecyclopropane and 1,2-dimethylcyclopropene (reactions S and V in Scheme 1) in glacial acetic acid at 298 K brings about ring opening, resulting in a mixture of *cis*-dimethylcyclopropane, methylbutane, and *n*-pentane, the latter in a ratio of 2.3:1 as determined by GLC.[17] The experimental $\Delta_{hyd}H^{298}$ values for these two compounds in Table 1 have been calculated on the basis of hydrogen uptake, assuming that all hydrogen taken up went to produce *cis*-dimethylcyclopropane, methylbutane, and *n*-pentane.[17] Thus, the experimental uncertainty, particularly of reaction V, is larger than expected for hydrogenation calorimetry.

The unsigned arithmetic mean difference between five G2(MP2) $\Delta_{hyd}H^{298}$ results in Table 1 and the seven corresponding experimental results is 0.8 kcal mol^{-1}, and between G2(MP2,SVP) and experiment, it is 1.6 kcal mol^{-1}. With the exception of reaction V, which has a large experimental uncertainty, computed values are less exothermic than experimental values. These means are to be contrasted to 0.8 kcal mol^{-1} previously reported[1] for G2(MP2) calculations on reactions among C_4 hydrocarbons. In view of the scattered nature of the experimental results, and their rather large uncertainties, the equality

SCHEME 2



in G2(MP2) mean differences are probably not significant, except to show that the method does not become seriously defficient for C_4 as opposed to C_4 hydrocarbons. The G2(MP2,SVP) procedure is, as expected, less accurate than G2(MP2), particularly when the highly strained cyclopropyl moiety is treated.

Discussion

Knowing one $\Delta_f H^{298}$ of any one of the cyclic hydrocarbons in the set permits calculation of $\Delta_f H^{298}$ of all of the others as shown in Table 2. Of the 11 hydrocarbons in the set that remain after cyclopentene has been chosen as the standard, $\Delta_f H^{298}$ has been determined calorimetrically for five of them.

Cyclopentene was chosen as a reference point for calculating $\Delta_f H^{298}$ (Table 2) because it is near the center of the reaction system (Scheme 1). 1,2-Dimethylcyclopropane might have been a more desirable choice, but we felt that its thermochemistry is not sufficiently well established for use as a reference. Criteria for a reference compound are (1) that it be connected to all other compounds in the scheme by the smallest number of reactions (to minimize cumulative error) and (2) that its thermochemistry, including sample stability and purity, be well-defined and reliable. $\Delta_f H^{298}$ was calculated by the usual convention $\Delta_{hyd} H^{298} = \Delta_f H^{298}(\text{product}) - \Delta_f H^{298}(\text{reactant(s)})$, recalling that $\Delta_f H^{298}(H_2) \equiv 0$.

The standard references[19] do not list experimental $\Delta_f H^{298}$ values for *cis*- and *trans*-1,2-dimethylcyclopropane in the gaseous state, but accurate liquid-phase values are -6.29 ± 0.16 and -7.34 ± 0.19 kcal mol^{-1}, respectively.[20a] The enthalpy of vaporization of 1,1-dimethylcyclopropane is[20b] 6.00 ± 0.20 kcal mol^{-1}, and its $\Delta_f H^{298} = -7.97$ kcal mol^{-1}. Taking $\Delta_{vap} H^{298}$ of the 1,2-dimethylcyclopropenes to be approximately the same as the 1,1- isomer, the gas-phase $\Delta_f H^{298}$ are -0.3 ± 0.4 and -1.3 ± 0.4 kcal mol^{-1} as listed in Table 2.

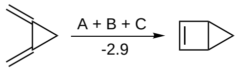
The unsigned arithmetic mean deviation between calculated and experimental results in Table 2 is 0.5 kcal mol^{-1} for the G2(MP2) method and 1.1 kcal mol^{-1} for the G2(MP2,SVP) method. Both G2(MP2) and G2(MP2,SVP) results have an arithmetic mean signed deviation from experiment that is smaller than the arithmetic mean unsigned deviations, showing some randomness, i.e., arguing against a systematic error. We believe that this randomness probably results from the scatter in experimental data, not from the computations.

Errors in the computational results in Table 2 are difficult to evaluate because of uncertainties in the experimental data already mentioned, but we believe that, even allowing for some fortuitous coincidence between experiment and calculation, there has been no diminution in reliability between C_4 hydrocarbons studied previously and the C_5 hydrocarbons reported here.

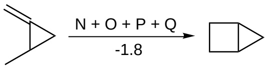
Substantial structural changes occurring in the reactions shown in Scheme 1 cause the assumptions $\Delta C_p \cong 0$ and $\Delta\Delta H^{298} \cong 0$ to break down. Thus, obtaining $\Delta_{isom} H^{298}$ and $\Delta_{hyd} H^{298}$ from $\Delta_{isom} E^0$ and $\Delta_{hyd} E^0$ by the approximations $\Delta\Delta_{isom} H = 0$ and $\Delta\Delta_{hyd} H = -1.9$ kcal mol^{-1} gives poor results for reactions I, K, W, and Y in which the size of the ring changes from five to three or the reverse. The approximate rule for temperature conversion should be revised to "$\Delta_{isom} H$ and $\Delta_{hyd} H$ change by 0 and -1.9 kcal mol^{-1} between 0 and 298 K *in the absence of substantial structural changes concomitant with the reaction*".

Compounds in Scheme 1 are arrayed according to their $\Delta_f H^{298}$ values in Scheme 2. In Scheme 2 the energetic advantage of exocyclic methylene unsaturation over endocyclic cyclopropene can be seen, as can the *trans* advantage over *cis* in the dimethylcyclopropanes and the methyl stabilization of 1,2-dimethylcyclopropene relative to 1,3-dimethylcyclopropene. The most dramatic stabilization is, as expected, that of a five-membered ring relative to the several 3-membered rings.

It is noteworthy that the isomerizations



and



are nearly energetically null at 298 K.

Also noteworthy are the *endothermic* hydrogenations lettered I and K in Scheme 1, in which the normally exothermic addition of H_2 is more than counterbalanced by the enthalpic expense of shrinking a five-membered ring to a three-membered ring. The highly endothermic isomerization Q has a similar explanation. Endothermic hydrogenations are known, based on reactant stability, as in the case of

$$\text{benzene} \rightarrow \text{cyclohexa-1,3-diene}$$

but the endothermic ΔH^{298} is not so large as reaction I. The hydrogenation L is as exothermic as an alkyne hydrogenation (~69 kcal mol^{-1}) because of the enthalpic release on opening the three-membered ring in bicyclo[2.1.0]pent-2-ene. The simple ring opening Y is less exothermic than opening the unsaturated ring in L by 14 kcal mol^{-1}.

We have taken up the study of methylcyclobutene and similar hydrocarbon systems and cyclic and acyclic heteroatomic molecules as well. We hope to investigate other *ab initio* methods such as density functional and complete basis set calculations[21] with the objectives of computer resource economy and the study of larger molecules.

Conclusion

In conclusion, and in answer to the questions posed in the Introduction, we find that (1) the G2(MP2)$\Delta_{\text{hyd}}H^{298}$ method has been successfully extended to 12 C_5 hydrocarbons, (2) there is little or no decrease in accuracy in G2(MP2) results as judged from comparison with a somewhat sparse set of experimental results, and (3) the G2(MP2,SVP) method agree less well with experiment than G2(MP2) but results are still within an acceptable margin of about 1 kcal mol^{-1}. We feel that these results show that calculation of $\Delta_f H^{298}$ through $\Delta_{\text{hyd}}E_0$ and $\Delta_{\text{isom}}E_0$ by methods in the G2 family and *ab initio* procedures of similar accuracy are of general utility for small, cyclic hydrocarbons.

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Supporting Information Available: Tables of calculated G2 and G2MP2 Enthalpies of C_5 Hydrocarbons and details of the 6-31G(d) MP2 and optimized geometries of all molecules in Scheme 1 (6 pages). Ordering information is given on any current masthead page.

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