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HEATS OF HYDROGENATION AND FORMATION OF SOME 5-MEMBERED RING COMPOUNDS BY MOLECULAR MECHANICS CALCULATIONS AND DIRECT MEASUREMENTS

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Abstract—Molecular mechanics calculations (MM2) have been carried out on twenty hydrocarbons, all of which are either cyclopentenes or alkylidenecyclopentanes. The heats of hydrogenation of eight of these compounds were measured in hexane solution at room temperature. These calculated and experimental results are compared with available heats of formation, determined primarily from combustion data. The agreement between the hydrogenation values and the molecular mechanics values is in general quite good, the agreement with the combustion data somewhat less so.

CYCLOPENTENE, substituted cyclopentenes and related compounds pose some interesting thermochemical and structural problems. The possibility of *cis–trans* isomerism in the reaction product obtained by hydrogenating, e.g. 1,2-dimethylcyclopentene, makes the thermochemistry of hydrogenation more complicated than most of what is in the existing literature.[1] The problem of *exo*- and *endo*-unsaturation has been the subject of continuing study[2–5] as has the molecular mechanical problem of puckering of the cyclopentene ring and interaction of Me groups when attached to a small ring.[6]

Literature values for the enthalpies of formation of cyclopentene derivatives, particularly heats of formation derived from combustion studies, are fragmentary and somewhat contradictory.[7] Accordingly, we have generated the molecular mechanical enthalpies of formation for cyclopentene and some related compounds. We have determined the enthalpy of hydrogenation of some representative ones so as to compare them with the molecular mechanical results and with existing combustion data.

EXPERIMENTAL

Apparatus. Recent changes in the calorimeter have been described[8] with references to some more detailed explanations. The electronics were the same as those previously used[8] except that a 100 k ohm protective shunt resistor was placed across the input to the recorder. Another minor change was replacement of the styrofoam insulating well with a polyurethane blanket, 5 cm thick, cut and cemented to a styrofoam base. The blanket was cut in such a way that the calorimeter can be pressed into a central well, leaving nothing exposed except the septum, where it is held fast by the elastic polyurethane. The styrofoam base was then cemented to the top surface of a magnetic stirrer. This arrangement eliminates the use of clamps and any conductive heat leak they might cause.

Reagents. All samples were obtained from Chemical Samples Company, 4692 Kenny Road, Columbus, Ohio, and are guaranteed to be 99% pure or better. Several were 99.8 or 99.9% pure (see catalog) but methylene cyclopentane was 98% pure or better. The standard, 1-hexene, came from the same source and was 99.9% pure. The calorimeter fluid and solvent for samples and standard was Baker analyzed "Hexanes" and as the name implies was not chromatographically homogeneous, showing a very narrow split peak on analysis using a SE 30 capillary column.

Procedure. Sample size was reduced from 600–700 mg per 10.00 ml to 200–300 mg diluted to 2.00 ml. The remainder of the procedure was identical to what has been described.[8] GLC verification of completeness of reaction consisted of observation of a single clean peak in addition to the split solvent peak. The reaction product from the methylcyclopentenes and methylenecyclopentane (presumably methylcyclopentane) was not cleanly separated from the solvent peak. In one case, ethylidinecyclopentane, a small peak at shorter retention time than the product peak indicated about 1% of an impurity in the reaction product. The product from 1,2-dimethylcyclopentene showed *cis*- and *trans*-1,2-dimethylcyclopentanes. Separation is good using a 300′ SE 30 capillary column. The isomers were identified by comparison with authentic samples also obtained from Chemical Samples Co. The *cis*- isomer has the longer retention time of the two.

RESULTS AND DISCUSSION

Molecular mechanics results[9]. Cyclopentene was calculated (MM2) to be in the envelope conformation (C_s), with bond lengths of 1.338, 1.504 and 1.543 Å. The interior ring angles at carbons 2, 3 and 4 are, respectively, 112.1, 101.8 and 106.2°. This gives a dihedral angle 1-2-3-4 of 15.0°. The barrier to planarity is 0.60 kcal mol^{-1}, and the heat of formation and strain energies are, respectively, 8.72 and 7.60 kcal mol^{-1}, all in reasonable agreement with experiment.[20] The calculated and experimental heats of hydrogenation for this and the other compounds discussed below are given in Table 1. The heats of formation are given in Table 3, from the molecular mechanics calculations, from combustion measurements, and from heats of hydrogenation. For cyclopentene these numbers are all in good agreement. The 1-Me derivative seems unexceptional. The 3-Me derivative has two possible conformations, with the Me in either an equatorial or an axial position. The equatorial

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Table 1. Heats of hydrogenation determined directly and calculated by molecular mechanics.

	Direct	Mol. Mech.	Dir - MM
Cyclopentene	-26.94 ± 0.13	-26.91	.03
1-Methylcyclopentene	-24.22 ± 0.12	-24.33	-.11
3-Methylcyclopentene	-27.58 ± 0.18	-27.15	.43
4-Methylcyclopentene	---	-26.43	---
1-Ethylcyclopentene	-24.36 ± 0.15	-24.29	-0.07
3-Ethylcyclopentene	-27.37 ± 0.11	-26.94	0.43
4-Ethylcyclopentene	---	-26.05	---
1,2-Dimethylcyclopentene	-22.55 ± 0.18	-22.49	.06
1,4-Dimethcyclopentene	---	-23.49	---
1,5-Dimethcyclopentene	---	-24.82	---
trans-3,4-Dimethylcyclopentene	---	-26.60	---
cis-3,4-Dimethylcyclopentene	---	-25.78	---
trans-3,5-Dimethylcyclopentene	---	-26.44	---
cis-3,5-Dimethylcyclopentene	---	-26.94	---
Methylenecyclopentane	-27.70 ± 0.23	-28.97	-1.27
Ethylidinecyclopentane	-25.56 ± 0.10	-26.38	-0.82

position is more stable, with a dihedral angle 1-2-3-Me of 138.9°, and an energy 0.21 kcal mol^{-1} below that of the axial, which has the dihedral angle 103.4°.

The 4-methylcyclopentene also has axial and equatorial conformations, with dihedral angles 2-3-4-Me of 98.7 and 149.3°, respectively, and the equatorial is more stable by 1.01 kcal mol^{-1}.

1-Ethylcyclopentene has three conformations; the Me group can either eclipse the double bond, or one of the hydrogens on the methylene can eclipse the double bond, in which case the Me group is either above or below the ring plane, on the same or opposite side of the plane from the C4 methylene. In 1-butene, the conformation with the Me eclipsing the double bond is somewhat higher in energy than the *gauche* conformations, but in this molecule it is found that the conformation with the Me eclipsing the double bond is in fact the most stable, with the other conformations being 0.16 kcal mol^{-1} higher in energy (when the Me is on the opposite side of the ring plane from the C4 methylene), and 0.32 kcal/mol higher when the Me and the C4 methylene are on the same side of the plane. The contrast relative to the open chain seems to come about because the 5-membered ring opens out the angle 2-1-6 in the *gauche* conformation, compared with the open chain. When the cyclopentene derivative goes from the *gauche* conformation to the eclipsed conformation, very little additional angle opening and very little increase in bending energy are required, whereas these changes are much larger with the open chain.

3-Ethylcyclopentene is a mixture of six conformations, where the Me of the Et can rotate into any of three places, and the Et can be attached at an axial or at an equatorial position. The most stable conformation has the equatorial Et, and the Me is *anti* to carbon 2.

With the 4-ethylcyclopentene, there are again six conformations, of which two are mirror images of two others. The Et can be axial or equatorial, and the latter is more stable. The Me of the Et can be located either on the C_s plane, or in the unsymmetrical position, and the latter is more stable in each case.

1,2-Dimethylcyclopentene has only one conformation, which seems unexceptional. The 1,4-dimethyl derivative has two conformations, with the 4-Me equatorial or axial, as with 4-methylcyclopentene itself. The former is in the dimethyl case more stable by 0.97 kcal/mol.

With 1,5-dimethylcyclopentene, the Me at C_5 has an inherent tendency to be equatorial, but in such a position it has an unfavorable repulsion with the Me at C_1. If the Me at C_5 is axial, it avoids this repulsion with the other Me, but at the expense of being axial. These two energy effects exactly cancel, and the two conformations are equally stable.

3,4-Dimethylcyclopentene has *cis* and *trans* isomers.

Table 2. Comparison of old and new data for four key compounds.

Compound	Turner	Old	New
Methylenecyclopentane	-26.85 ± 0.05	-26.2 ± 0.3	-27.70 ± 0.23
1-Methylcyclopentene	-23.01 ± 0.05	---	-23.99 ± 0.06
Ethylidenecyclopentane	-24.88 ± 0.12	-24.2 ± 0.2	-25.45 ± 0.10
1-Ethylcyclopentene	-23.56 ± 0.11	-23.5 ± 0.2	-24.36 ± 0.15

Table 3. Heats of formation (gas phase, 25°C) from combustion, molecular mechanics and heats of hydrogenation. Heats of formation are calculated from hydrogenation data by Hess' Law addition to combustion data for the heat of formation of the product cycloalkane.

Compound	Source of Data Combustion	Calculation	Hydrogenation
Cyclopentane	-18.44	-18.26	
Methylcyclopentane	-25.27	-25.58	
1,2-Dimethylcyclopentane, trans-	-32.66		
cis-	-30.95		
Ethylcyclopentane	-30.34	-30.53	
Cyclopentene	8.23	8.65	8.50
1-Methylcyclopentene	-0.86[a]	-1.25	-1.05
3-Methylcyclopentene	1.76[a]	1.57	2.31
4-Methylcyclopentene	3.5	0.85	
1-Ethylcyclopentene	-4.72[a]	-5.88	-5.98
3-Ethylcyclopentene	---	-3.24	-2.97
4-Ethylcyclopentene		-4.12	
1,2-Dimethylcyclopentene		-10.17	-9.89
1,4-Dimethylcyclopentene		-8.99	
1,5-Dimethylcyclopentene		-7.84	
3,4-Dimethylcyclopentene, trans-		-6.06	
cis-		-5.17	
3,5-Dimethylcyclopentene, trans-		-5.48	
cis-		-5.54	
3,3-Dimethylcyclopentene		-6.41	
4,4-Dimethylcyclopentene		-6.98	
Methylenecyclopentane	2.78 ± 0.5[b]	3.39	2.43
Ethylidinecyclopentane	-4.33[a]	-4.15	-4.78

a) $H_f^0(g)$ from ref. 5; all others from ref. 7.

b) The liquid phase value if from ref. 7, and we have estimated the heat of vaporization to be the same as that of methylcyclopentane.

For the *cis* isomer, the Me at C_4 dominates the situation. It achieves an equatorial conformation, forcing the Me at C_3 into an axial position. The difference in energy between these conformations is 1.16 kcal mol^{-1}. From the monomethylcyclopentenes, the conformational energies of the Me are 0.21 and 1.01 kcal/mol in the 3 and 4 positions respectively. If these quantities were additive in the *cis* isomer, the energy difference would be 0.80, favoring the C_4 equatorial conformation, so the additivity is not exact, but is close.

With the *trans* isomer, both Me's are axial, or both are equatorial. The diequatorial conformation is more stable by 1.04 kcal mol^{-1}. This number is not larger because of the somewhat unfavorable interaction between the Me's in the diequatorial conformation which is relieved in the diaxial. The *trans* isomer is more stable than the *cis* by 0.89 kcal mol^{-1}.

3,5-Dimethylcyclopentene exists in *cis* and *trans* isomers. The *trans* isomer has a single conformation, one Me is axial and one is equatorial. The *cis* isomer has two conformations, diaxial and diequatorial. These latter differ by 0.74 kcal mol^{-1}, the diequatorial being more stable. Although the diequatorial conformation of the *cis* isomer is more stable than the *trans* isomer by 0.22 kcal mol^{-1} when the conformational mixture of the *cis* isomer is considered, it has a lower enthalpy than the *trans* by only 0.06 kcal mol^{-1}.

The 3,3- and 4,4-dimethylcyclopentenes were also studied, and they each have a single conformation with no unusual features.

Heats of hydrogenation. The heats of hydrogenation calculated by molecular mechanics for sixteen unsaturated compounds, together with the results of direct measurements for eight of the group, are shown in Table 1. Each experimental datum represents 6 or 9 replicate experimental runs. The 95% confidence limits shown were computed from the standard deviation of all experimental runs for either 5 or 8 degrees of freedom, as appropriate. Since these are confidence limits on aliquot samples of the same solution, they do not include weighing or dilution errors. In each case, the entire experiment was run in duplicate or triplicate to guard against undetected systematic errors. Our present estimate of the confidence limits including all sources of error is ±0.3 kcal $mole^{-1}$ for stable, nonvolatile monoalkenes.

There is obvious advantage to small sample size for many compunds which are expensive or difficult to purify. This method uses only 200–300 mg total sample diluted to 2.00 mL of total solution. Each 40 μL aliquot of the 6 or 9 experimental runs used to give each mean in Table 1 contains approximately 4 mg of sample, thus the lower limit of total sample size has not been reached. We feel at present that we can confortably and reliably handle total samples of 200 mg, the principal limiting factors being weighing and dilution. Each aliquot produces about 1.8 calories of heat and causes a temperature rise of a little less than 0.15°.

In the case of cyclopentene, the entries shown were obtained in different laboratories about a year apart, by different investigators, using different apparatus. Cyclopentene has become something of a test substance for hydrogen calorimetry, having been studied first by Kistiakowsky[10] who obtained $\Delta H_h = -26.92 \pm 0.06$ kcal $mole^{-1}$ at 82° in the gas phase. Turner's group obtained -26.04 ± 0.44 kcal $mole^{-1}$ for 12 determinations taken over a 10 yr period on aliquot portions of the same sample.[11] The meaning of the 0.44 kcal $mole^{-1}$ uncertainty estimate is not clear in the original publication but this number is probably a standard deviation. We obtained an early value[4] of -26.2 ± 0.2 kcal $mole^{-1}$. Both Turner's value and ours are heats of hydrogenation in glacial acetic acid, a measurement which is complicated by endothermic solution effects. The way in which the various heats of solution enter into the heat of hydrogenation differs, however, because of different experimental procedures used by the two groups.

Our early work involved addition of cyclopentene to calorimeter fluid which was agitated to form a slurry with Pd catalyst coated on activated charcoal. The heat produced is the algebraic sum of the exothermic enthalpy of hydrogenation and the endothermic heat of solution of cyclopentane in acetic acid. Thus the magnitude of the measured enthalpy change should be increased by the heat of solution of cyclopentane to give the desired "corrected" heat of hydrogenation.

Turner's experimental strategy[12] leads to a solution correction which is smaller than ours but not zero. His group mixed a weighed sample of cyclopentene with glacial acetic acid and allowed the system to come to thermal equilibrium. After thermal equilibrium had been established, an ampoule containing catalyst was broken into the mixture causing the reaction to take place. The obvious correction, subtraction of the exothermic heat of activation of the catalyst from the heat of hydrogenation, was made, but a less obvious one was not. When cyclopentene is mixed with glacial acetic acid, an exothermic Lewis acid-base reaction takes place between sample and solvent. When hydrogenation occurs, the product alkane is not associated as an acid-base pair with the solvent so that the apparently simple hydrogenation reaction actually consists of two processes, hydrogenation and an endothermic dissociation of the acid-base pair formed between the reactant and the solvent. The endothermic correction factor is the difference between the heats of solution of the alkane and the alkene.

We have constructed a microcalorimeter for determining heats of solution and other small heat effects.[13] Our examination of cyclopentene and cyclopentane solutions in glacial acetic acid produced 0.57 ± 0.03 kcal $mole^{-1}$ for the heat of solution of cyclopentene and 1.18 ± 0.06 kcal $mole^{-1}$ for the heat of solution of cyclopentane. The correction for our early datum is 1.18 kcal $mole^{-1}$ which leads to -27.4 ± 0.4 kcal $mole^{-1}$ for the heat of hydrogenation of cyclopentene. The correction factor to be applied to Turner's datum (mean) is 0.61 kcal $mole^{-1}$ which leads to -26.65 ± 0.5 kcal $mole^{-1}$ for his corrected heat of hydrogenation. Our mean H_h, shown in Table 1, is the arithmetic mean of -26.84 ± 0.07 for one set of experimental runs and -27.03 ± 0.19 kcal $mole^{-1}$ for the other. Both sets of experiments were carried out using hexane as the calorimeter fluid, hence no heat of solution correction has been made. Four of these five determinations, Kistiakowsky's, Turner's corrected mean, and both of our recent uncorrected means are statistically indistinguishable, having a range of 0.38 kcal $mole^{-1}$ and a mean of -26.83 kcal mol^{-1}.

Our early value for the heat of hydrogenation of cyclopentene in acetic acid appears, when the appropriate correction factor is applied, to be about 0.4 kcal/mol too exothermic. This is within the stated reliability limits (±1.0 kcal $mole^{-1}$) in the original paper but not within the ±0.3 kcal $mole^{-1}$ error estimate of the present work. It is interesting to note how closely grouped the results are for the liquid–liquid transition at 25° and how close they are to the gas phase value obtained at 82°. The heat of vaporization of cyclopentene[14] is 6.71 ± 0.07 kcal $mole^{-1}$ and that of cyclopentane[15] is 6.85 ± 0.01 kcal $mole^{-1}$ which should make the gas phase hydrogenation 0.14 kcal $mole^{-1}$ *less* exothermic than the liquid phase reaction. Application of Kirchoff's equation[16] to the addition of hydrogen to cyclopentene using interpolated heat capacities[17] at the mean reaction temperature of 53.5° leads to a ΔCp of -4.63. Multiplying this into the temperature range of 57° yields 264 calories *increase* in the magnitude of the heat of hydrogenation of cyclopentene on going from the lower to the higher temperature. These corrections are in opposite directions and partially cancel. Hence we calculate that the heat of the gas-phase hydrogenation should be only about 0.12 kcal $mole^{-1}$ larger in magnitude at 82° than the heat of the liquid phase hydrogenation at 25°. The $\Delta Cp \Delta T$ correction will always be small, usually smaller than experimental error[1] but the difference in heats of vaporization may be much larger.[18] Unfortunately many heats of vaporization of interest are known inaccurately or not at all.

Table 2 shows the heats of hydrogenation of four key compounds determined by Turner, by our old method, and by our new method. In view of the systematic endothermic solution effects inherent in Turner's data and the less precise apparatus used in our earlier work, it is our opinion that the new values should replace all of the older ones.

Hess' law subtraction of the heat of hydrogenation of 1,2-dimethylcyclopentene from the heat of formation of *trans*-1,2-dimethylcyclopentane gave a thermochemical heat of formation of the alkene which is in fairly good agreement with the result from molecular mechanics but the same calculation using ΔH_f for the *cis* product gave a poor result. In addition, 1,2-dimethylcyclopentene is kinetically slightly slower to hydrogenate than cyclopentene and the monosubstituted derivatives.

Heterogeneous catalytic hydrogenation to give a *trans* product is not uncommon.[19] The present case probably involves a preliminary migration of the double bond away from the tetrasubstituted position, followed by hydrogenation at some site other than that between the two Me-substituted carbons. The product of hydrogenation would not then necessarily be either *cis* or *trans* but probably a mixture. Migration away from a tetrasubstituted C-C double bond to an adjacent site, followed by hydrogenation of the latter, is probably a common occurrence in catalytic hydrogenation.

cis- and *trans*-Dimethylcyclopentane can be separated by GLC, but the hexane we usually use as a calorimeter fluid contains some (probably isomeric) impurities which might be confused with one or the other of the expected reaction products. Hence, we re-ran the experiment using very pure pentane as the calorimeter fluid, which, aside from the advantage of its purity, would be expected to show better separation from the product peaks. The resulting chromatogram (SE 30 at ambient temp) showed, aside from the solvent peak at short retention time, two product peaks, a large one at intermediate retention time, and a small one at longer retention time. The area ratio of the peaks was 6.4 to 1. Addition of an authentic sample of *cis*-dimethylcyclopentane to the reaction mixture augmented the smaller of the two peaks, and hence we conclude that the reaction product was 86% *trans*.

Treating the product as having a weighted average of the heats of formation of the *cis* and *trans* isomers, one can calculate the heat of formation of 1,2-dimethylcyclopentene as 9.89 kcal/mol (Table 3). This number leads to the heat of hydrogenation of the 1,2-dimethylcyclopentene to give the pure *trans* isomer (−22.8 kcal mole^{-1}) or the similar heat of hydrogenation to give the pure *cis* isomer (−21.1 kcal mole^{-1}).

Deviations between calculated and observed heats of hydrogenation are shown in the rightmost column of Table 1. The average signed deviation of the first six results is +0.13 kcal mole^{-1} indicating no significant systematic deviation. The largest deviations are +0.43 kcal mole^{-1} for 3-methylcyclopentene and 3-ethylcyclopentene, which are within the combined confidence limits of the two methods. A slight error in parameterization in the 3 position is suggested but not demonstrated. On the other hand, the remaining two results, those for methylenecyclopentane and for ethylidenecyclopentane are outside the combined confidence limits and both deviations are in the same direction. In view of the results in Table 2 and the discussion on solvent corrections of Turner's results, the experimental data appear to be reliable and the problem seems to be in parameterization of the molecular mechanical force field for the C=CH_2 moiety.

When the parameterization was carried out, the experimental value for the heat of formation of methylenecyclopentene available was 3.36 kcal mol^{-1}. The current value is 2.78 kcal mol^{-1}, or 0.58 kcal more negative. Use of this newer value in the parameterization would have reduced the calculated heat of formation by an amount between 0.00 and 0.58 kcal mol^{-1}. (It cannot be told where in this range the result would be without repeating the optimization, and the parameterization is fixed and published, so we do not feel this would be worthwhile now). This would in turn reduce the magnitude of the error (1.27 kcal) by up to 0.58 kcal mol^{-1}, and the error in the ethylidenecyclopentane by a similar amount. Thus it seems likely that a significant part of the error in these two compounds stems from inaccurate parameterization, which in turn stems from inaccurate early experimental data.

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