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Accuracy of Calculations of Heats of Reduction/Hydrogenation: Application to Some Small Ring Systems

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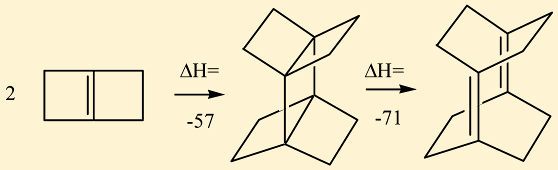
S Supporting Information

ABSTRACT: The enthalpies of reduction of carbonyl compounds and hydrogenation of alkenes have been calculated at the HF, B3LYP, M06, MP2, G3, G4, CBS-QB3, CBS-APNO, and W1BD levels and, in the case of the first four methods, using a variety of basis sets up to aug-cc-pVTZ. The results are compared with the available experimental data, and it is found that the compound methods are generally more satisfactory than the others. Large basis sets are usually needed in order to reproduce experiments. Some C−C bond hydrogenolysis reactions also have been examined including those of bicycloalkanes and propellanes. In addition, the dimerization of the remarkably strained bicyclo[2.2.0]hex(1,4)ene was studied. The reaction forming a pentacyclic propellane was calculated to have Δ*H* = −57 kcal/mol, and the cleavage of the propellane to give a diene had Δ*H* = −71 kcal/mol. The strain energies of these compounds were estimated.



1. INTRODUCTION

The heats of formation are one of the principle quantities required for completely characterizing compounds. These data are useful in studying a variety of reactions and in making estimates of whether or not a reaction may occur. Currently, there are few precise thermochemical measurements being carried out, and computational methods have been developed to fill the breach. Compound methods have become popular for this purpose, and examples include Pople's G series,[1] Petersson's CBS methods,[2] Martin's W1 method,[3] and others.[4] They will generally give heats of formation with an average error of ∼1−2 kcal/mol or better and also provide estimates of the free energy of reaction.

The quality of these methods is generally assessed by a comparison of calculated and observed heats of formation for a test set of molecules. Another method would make use of the calculated total enthalpies. Since all are variationally bound (except for some small semiempirical corrections), the best method should usually yield the lowest total enthalpy. Such a comparison for acetone is given in Table 1. The differences are substantial since 1 H = 627.51 kcal/mol.

One might expect that heats of reaction could be calculated with a smaller error than heats of formation as a result of some cancellation of errors. This might especially be the case for enthalpies of hydrogenation where the reactant and product are quite similar in structure. These enthalpies of reduction are particularly useful in this context since there is a considerable body of experimental result and the enthalpies may be obtained in several ways.

Table 1. Calculated Total Enthalpies for Acetone

method	H
CBS-QB3	−192.81411
G3B3	−192.99480
G4	−193.02176
CBS-APNO	−193.06123
W1BD	−193.14254

2. RESULTS AND DISCUSSION

2a. Reduction of Carbonyl Compounds. We have first examined the reduction of carbonyl compounds,[5] and Table 2 gives the experimental results for a group of small aldehydes and ketones. Here, column A gives the enthalpies derived from gas-phase hydrogenations,[6] column B gives values obtained via heats of reduction of the carbonyl compounds using triethylaluminum hydride in diglyme,[7] columns C and D give enthalpy changes derived from the equilibrium constant for the hydrogenation reaction in the gas phase,[8] and column E gives the independently determined difference in enthalpy between the carbonyl compound and the hydroxyl product as obtained via combustion calorimetry.[9]

The enthalpy of hydrogenation of acetone has been measured in four different ways, giving remarkable agreement. Therefore, we have used it as the test compound for a series of different calculations that are summarized in Table 3. It includes B3LYP[10] that is one of the oldest, but still widely used, hybrid DFT methods, and M06[11] that is one of the more recent methods. MP2 was included because it is one of the most frequently used ab initio methods that include correction for electron correlation. Basis sets include 6-311+G*, 6-311++G**, and aug-cc-pVTZ.[12] The first is fairly flexible with diffuse (+) functions and polarization functions (*) at the non-hydrogen atoms and the second includes them on all af the atoms. The

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Table 2. Experimental Enthalpies of Hydrogenation of Carbonyl Compounds, 298 K

compd	A	B	C	D	E
formaldehyde					−22.1 ± 0.1
acetaldehyde	−16.5 ± 0.1	−15.4 ± 0.3			
propanal		−15.9 ± 0.1	−15.7 ± 0.2		−16.6 ± 0.2
butanal		−15.1 ± 0.1	−16.9 ± 0.3		−16.8 ± 0.3
2-methylpropanal		−16.3 ± 0.3		−16.3 ± 0.2	−16.2 ± 0.3
acetone	−13.2 ± 0.1	−13.0 ± 0.1	−13.2 ± 0.1		−13.3 ± 0.2
cyclobutanone		−12.7 ± 0.3			
cyclopentanone	−12.3 ± 0.2	−10.9 ± 0.2			−11.6 ± 0.6
cyclohexanone	−15.2 ± 0.2	−14.1 ± 0.2			−14.4 ± 0.7
cycloheptanone		−10.9 ± 0.3			
cyclooctanone		−9.3 ± 0.3			
ethyl acetate		−6.0 ± 0.2			−6.4 ± 0.2

Table 3. Effect of Computational Level on the Calculated Enthalpy of Reduction of Acetone

level	ΔH(298 K) (kcal/mol)	rel CPU time[a]
HF/6-311+G*	−8.3	1
HF/aug-cc-pVTZ	−10.1	106
B3LYP/6-311+G*	−7.1	2
B3LYP/6-311++G**	−10.0	4
B3LYP/aug-cc-pVTZ	−10.1	90
M06/6-311+G*	−9.4	4
MM06/6-311++G**	−12.7	6
M06/aug-cc-pVTZ	−11.5	250
MP2/6-311+G*	−6.6	3
MP2/6-311++G**	−12.8	7
MP2/aug-cc-pVTZ	−14.5	500
CBS-QB3	−12.6	5
G4	−13.1	60
CBS-APNO	−13.5	55
W1BD	−14.1	2700
expt	−13.2 ± 0.2	

[a] These times are for acetone and are only approximate since they depend on the time required to optimize the starting structures. They had first been optimized at a lower level. The relative times for isopropyl alcohol are about the same. The long execution times for DFT and MP2 using the largest basis set are largely due to the time needed to calculate the vibrational frequencies.

aug-cc-pVTZ basis set is considerably larger and is of triple-ζ quality.

Results are also given for the compound methods. Table 3 includes approximate relative CPU times for these methods including the calculation of the vibrational frequencies. Small differences are insignificant since the time will depend on that required to optimize the initial structure. But it is clear that going from 6 to 311+G* to aug-cc-pVTZ increases the total time for acetone by about 50−100. With the compound methods, CBS-QB3 required little more time than MP2 using the smaller basis set. CBS-APNO increased the execution time relative to CBS-QB3 by about 10, and W1BD increased it by about 500. The relative times will depend on the molecule studied since different methods respond differently to the size of the molecule.

With all of the methods used, there were significant changes in calculated reduction enthalpies on going from the fairly flexible 6-311+G* basis set to the larger 6-311++G** and the much more flexible aug-cc-pVTZ. The energy changes calculated using the former basis set were in poor agreement with the observed value, indicating the importance of the choice of basis set. The DFT values, even with the larger basis set, had a 2−3 kcal/mol error.

The large basis set MP2 calculation and the G4, CBS, and W1BD calculations gave satisfactory agreement with the experimental value. However, it would not be appropriate to choose between them based on only one compound. Therefore, we have examined a variety of small aldehydes and ketones along with ethyl acetate (Table 4). These compounds do present conformational problems that need to be addressed. The product alcohol generally can adopt one of

Table 4. Calculated Enthalpies of Reduction of the Lowest Energy Carbonyl Conformers (kcal/mol)

compd	B3LYP[a]	M06[a]	MP2[a]	QB3	G3B3	G4	APNO	W1BD	obsd[9]
$H_2C{=}O$	−20.6	−21.6	−22.4	−20.4	−20.6	−21.0	−21.9	−22.6	−22.1 ± 0.1
MeCH=O	−14.0	−15.5	−17.2	−15.1	−15.5	−15.9	−16.2	−17.2	−16.5 ± 0.1
EtCH=O	−13.4	−15.1	−16.9	−15.0	−15.2	−15.6	−16.1	−16.8	−16.6 ± 0.2
nPrCH=O	−13.6	−15.1	−17.1	−15.2	−15.4	−15.8	−15.7		−16.3 ± 0.3
iPrCH=O	−14.0	−16.4	−17.7	−15.7	−15.9	−16.3	−16.9		−16.3 ± 0.3
Me2C=O	−10.1	−11.5	−14.5	−12.6	−13.2	−13.1	−13.5	−14.1	−13.2 ± 0.1
cyclopropanone	−25.0	−26.7	−29.8	−27.7	−27.8	−28.5	−28.9	−29.6	NA
cyclobutanone	−9.1	−12.0	−14.2	−12.1	−12.4	−12.9	−13.1		−12.7 ± 0.3
cyclopentanone	−7.0	−9.5	−11.8	−9.7	−9.9	−10.4	−10.4		−11.6 ± 0.6
cyclohexanone	−11.0	−14.2	−17.2	−14.0	−14.3	−14.5	−14.8		−14.4 ± 0.7
ethyl acetate	−6.4	−4.1	−6.1	−2.7	−3.9	−5.1	−5.1	−7.4	−6.4 ± 0.2
rms error	3.0	1.4	1.2	1.7	1.3	0.8	0.7	0.7	

[a] aug-cc-pVTZ calculations for both geometry optimizations and vibrational frequencies.

Table 5. Enthalpies of Hydrogenation of Alkenes, 298 K (kcal/mol), Using aug-cc-pVTZ for DFT and MP2

reaction	B3LYP	M06	MP2	CBS	G4	APNO	W1BD	expt
ethene + H_2 = ethane	−31.4	−34.8	−34.1	−31.8	−32.0	−33.5	−33.1	−32.5 ± 0.1
ethyne +$2H_2$ = ethane	−74.6	−77.5	−74.5	−73.4	−73.9	−76.4	−75.7	−74.5 ± 0.2
propene + H_2 = propane	−27.8	−31.8	−31.4	−29.1	−29.3	−30.6	−30.3	−29.8 ± 0.2
2-butene + H_2 = butane	−24.7	−28.6	−27.0	−26.8	−27.1	−28.1	−28.0	−27.3 ± 0.3
cyclopropene + H_2 = cyclopropane	−53.3	−54.1	−55.6	−54.0	−54.6	−55.7	−55.3	−53.5 ± 0.6
cyclobutene + H_2 = cyclobutane	−30.3	−34.1	−33.2	−31.3	−31.7	−32.9	−32.4	−30.8 ± 0.5
cyclobutadiene+H_2 = cyclobutene	−65.4	−68.5	−67.2	−63.6	−63.4	−65.2	−64.9	−64.8 ± 3.8
cyclopentene + H_2 = cyclopentane	−24.0	−27.7	−27.6	−25.6	−25.9	−27.9	−26.6	−26.4 ± 0.4
cyclopentadiene+$2H_2$ = cyclopentane	−45.2	−52.5	−51.0	−48.3	−49.0	−51.7	−50.6	−50.4 ± 0.4
cyc1ohexene + H_2 = cyclohexane	−25.3	−29.8	−29.7	−27.5	−27.9	−29.1		−28.3 ± 0.3
1,3-cyclohexadiene + $2H_2$ = cyclohexane	−49.0	−58.2	−56.8	−53.5	−53.3	−56.1		−55.0 ± 0.3
benzene +3 H_2 = cyclohexane	−38.2	−51.7	−47.0	−45.3	−47.1	−49.0	−49.8	−49.2 ± 03
bc[220]hex(1,4)ene + H_2 = bc[220]ane	−57.2	−60.6	−60.8	−59.1	−59.7	−60.9		na
rms error	4.4	2.4	1.7	1.5	1.1	1.3	1.0	

two conformations. With ethanol, for example, the hydroxyl hydrogen may be trans to the adjacent methyl group or it may adopt one of the energetically equivalent gauche conformations. The differences in energy are generally small, and for this part of the study we give the results for the lowest energy carbonyl compound going to the lowest energy product. The corrections that result from including the higher energy conformations may be found in the Supporting Information.

When the aug-cc-pVTZ basis set was used, most of the methods gave fairly satisfactory calculated enthalpies of reduction. B3LYP gave the largest deviations, followed by M06, with MP2 giving the more satisfactory results. The compound methods were generally more satisfactory, with CBS-APNO and W1BD giving the best results. Unfortunately, they also have the largest computational requirement. If making comparisons between calculations and experiments it should be remembered that the stated experimental uncertainties do not include the unknown systematic errors associated with most experiments

Although the observed values are well-known, there some are some aspects that deserve comment. Except for formaldehyde, all of the aldehydes have essentially the same enthalpies of reduction. The change in reaction enthalpies on going from formaldehyde to the other aldehydes, and then acetone parallel the changes in ease of hydration.[13] Formaldehyde is essentially completely hydrated in aqueous solution, acetaldehyde is partially hydrated, and acetone gives very little hydrate in aqueous solution. The stabilization of the carbonyl group by alkyl substitution is a reflection of the polar character of the C═O bond giving the carbon considerable carbocation character. Cyclobutanone, cyclopentanone, and cyclohexanone have enthalpies of reduction that are similar to that of acetone, but cyclopropanone[14] is more like formaldehyde and is completely hydrated in aqueous solution. Cyclopropane and cyclobutane have almost the same strain energies, but whereas the hydrogenolysis of cyclopropanone giving acetone has a calculated (CBS-APNO) $\Delta H = -56.6$ kcal/mol, the conversion of cyclobutanone to 2-butanone is much smaller with $\Delta H = -36.7$ kcal/mol. Clearly, a C═O group has more difficulty in accommodating a small ring angle than does a CH_2 group, but other factors may also be involved.[14]

3. HYDROGENATION OF ALKENES

The hydrogenation of C═C bonds is also of considerable interest. With the C═C bonds it is often possible to measure the gas-phase enthalpies of catalytic hydrogenation of volatile alkenes with considerable accuracy.[15] In other cases they were obtained from the heats of formation of the alkene and the alkane, and in the very interesting case of cyclobutadiene, it was measured via a set of gas-phase studies.[16] One might expect that these enthalpies might be more easily calculated than those for carbonyl compounds because there are negligible electronegativity differences and no lone pairs. The enthalpies have been calculated at a variety of theoretical levels giving the data summarized in Table 5. The DFT and MP2 calculations made use of the aug-cc-pVTZ basis set.

The conformers of the hydrocarbons are well-known,[17] and usually there is a large enough difference in energy so that only the lowest energy conformer need be considered. In the case of *n*-butane, the energies of both the trans and gauche forms were calculated (W1BD $\Delta H = 0.60$ kcal/mol, $\Delta G = 0.60$ kcal/mol), and the correction to the tabulated hydrogenation enthalpies is 0.2 kcal/mol.

Using aug-cc-pVTZ, there is relatively little difference in the values calculated using several methods. B3LYP gives too high enthalpies, whereas M06 gives values that are too negative. MP2 and CBS-QB3 are fairly satisfactory, but the best results were obtained using G4, CBS-APNO, and W1BD.

How will smaller basis sets affect the DFT and MP2 results? The enthalpies of reaction were calculated using 6-31G*, 6-311+G*, and 6-311++G**, and the results are summarized in Table 6.

The effect of basis set on the calculated enthalpies of hydrogenation is much smaller than found in the carbonyl reductions. The B3LYP values pass through the observed values; those for M06 are always too negative but improve with larger basis sets. The MP2 values are not as affected by the basis set size and are close to the observed value.

The change in enthalpies of reaction on going from ethene to propene and 2-butene is well-known and is presumably due to stabilization of the C═C group by methyl substitution. Cyclobutene, cyclopentene, and cyclohexene have similar enthalpies of reaction, but cyclopropene gives a much more exothermic reaction in part because of the strong CH bonds in the product.[18] Bicyclo[2.2.0]hex(1,4)ene is one of the most reactive of the alkenes that can be observed in solution,[19] and it gives a remarkably exothermic reaction. One of its reactions will be discussed in a subsequent section.

Table 6. Effect of Basis Set on the Calculated Enthalpies of Hydrogenation of Propene

level	ΔH(298 K) (kcal/mol)
B3LYP/6-31G*	−31.5
B3LYP/6-311+G*	−29.3
B3LYP/6-311++G**	−28.4
B3LYP/aug-cc-pVTZ	−27.8
M06/6-31G*	−34.2
M06/6-311+G*	−32.7
M06/6-311++G**	−32.2
M06/aug-cc-pVTZ	−31.8
MP2/6-31G*	−30.0
MP2/6-311+G*	−30.2
MP2/6-311++G**	−30.8
MP2/aug-cc-pVTZ	−31.4
observed	−29.8 ± 0.2

4. HYDROGENOLYSIS OF C−C BONDS

Unlike the above reactions, it is generally not possible to experimentally measure the enthalpies of hydrogenolysis of C−C single bonds. However, it is possible to obtain them from the heats of formation of the reactant and the product, and it is possible to calculate them. We have made use of CBS-QB3, G4, CBS-APNO, and W1BD for the calculations, and the values thus obtained are compared with the experimental data in Table 7.

For this group of reactions, all levels from G4 to APNO and W1BD give rather good agreement with the observed values. The cleavage of the Me-Me bond is more exothermic than that of the CH_2-CH_2 bond in butane, and the cleavage of the C−C bond in propane is halfway between these values as might be expected.

If one takes −10 kcal/mol as the "normal" value for the cleavage of a CH_2-CH_2 bond and subtracts this from the values found for the cycloalkanes, one obtains a result that closely agrees with the commonly assumed strain energies.[20] One might take the hydrogenolysis value for 2,3-dimethylbutane (−8 kcal/mol) as that for CH−CH, and then the strain energy of bicyclo[1.1.0]butane would be ~39 kcal/mol plus that of cyclobutane (~27 kcal/mol) or about 66 kcal/mol, that of bicyclo[2.1.0]pentane would be ~50 kcal/mol plus that of cyclopentane (~6 kcal/mol) or about 56 kcal/mol, and that of bicyclo[2.2.0]hexane would be ~53 kcal plus that of cyclohexane (~0) or about 53 kcal/mol. Thus, as noted previously, their strain energies are about the sum of the strain energies of the constituent rings.[20]

The hydrogenolysis enthalpy of hexamethylethane is more negative than that of 2,3-dimethylbutane, whereas it might be expected to be less negative on the basis of the effect of alkyl substitution from ethane to dimethylbutane. The difference probably reflects the strain introduced by the six opposing methyl groups. However, the small change suggests that the steric interaction is quite small.

The hydrogenolysis energy of [1.1.1]propellane (−39 kcal/mol) is relatively small because the product bicyclo[1.1.1]-pentane has a relatively high strain energy, and this is one factor that allows this propellane to be isolated.[21] On the other hand, the hydrogenolysis energy of [2.2.2]propellane (−90 kcal/mol) is quite large because bicyclo[2.2.2]octane is relatively unstrained, and this must be one factor that leads to the relative instability of the propellane.[22]

5. DIMERIZATION OF BICYCLO[2.2.0]HEX(1,4)ENE (A)

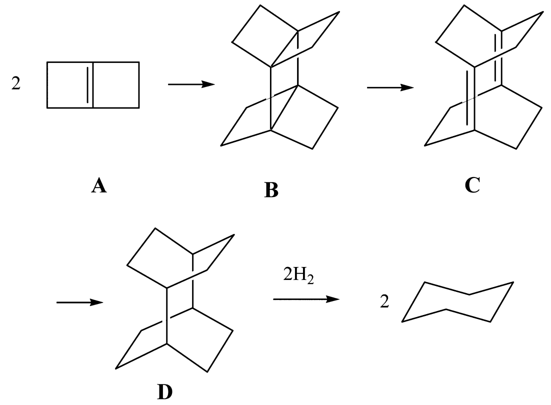
Although **A** can be prepared and its NMR spectrum can be obtained,[19,23] it undergoes fairly rapid dimerization even in dilute solutions to give the cyclic diene (**C**). It is among the most reactive alkenes that can be observed in solution. It is difficult to imagine a process for this conversion that does not involve the propellane **B** either as an intermediate or a transition state. The formation of **B** probably involves a diradical intermediate.[24] We were interested in obtaining an estimate of the energy changes that occur in the transformation. DFT calculations for these compounds have been reported,[19,24,25] but in view of the results given above, it seem desirable to reinvestigate them using CBS-QB3, G4, and CBS-APNO (Table 8).

The enthalpy change on going from **A** to **B** is quite remarkable considering that **B** is a propellane with five cyclobutane rings. **B** is certainly highly strained, and its conversion to **C** also is calculated to be very exothermic. The values in Table 8 are significantly larger than those observed

Table 7. Calculated Enthalpies of Hydrogenolysis, kcal/mol

reaction	QB3	G4	APNO	W1BD	obsd
ethane + H_2 → 2 methane	−12.7	−15.4	−15.5	−15.3	−15.6 ± 0.2
propane + H_2 → ethane + methane	−10.0	−12.7	−12.8	−12.8	−12.8 ± 0.2
butane + H_2 → 2 ethane	−7.2	−9.7	−10.0	−10.2	−10.0 ± 0.2
2,3-dimethylbutane + H_2 → 2 propane	−4.9	−7.2	−7.9		−7.4 ± 0.3
hexamethylethane + H_2 → 2 isobutane	−6.3	−8.5	−9.4		−10.2 ± 0.4
cyclopropane + H_2 → propane	−35.3	−37.5	−38.4	−38.3	−37.7 ± 0.1
cyclobutane + H_2 → butane	−33.9	−36.4	−37.0	−36.9	−36.6 ± 0.3
cyclopentane + H_2 → *n*-pentane	−14.3	−17.0	−15.5		−16.8 ± 0.3
cyclohexane + H_2 → *n*-hexane	−7.9	−10.7	−11.1		−10.4 ± 0.3
bicyclo[1.1.0]butane + H_2 → cyclobutane	−43.9	−46.2	−44.1	−47.6	−45.3 ± 0.4
bicyclo[2.1.0]pentane + H_2 → cyclopentane	−52.2	−54.3	−57.5		na
bicyclo[2.2.0]hexane + H_2 → cyclohexane	−57.4	−59.6	−60.6		na
[1.1.1]propellane + H_2 → bc[1.1.1]pentane	−35.9	−37.6	−37.9	−39.1	na
[2.2.2]propellane + H_2 → bc[2.2.2]octane	−86.2	−88.0	−91.1		na
biphenyl + H_2 → 2 benzene	1.2	−1.4			−4.0 ± 0.6
bibenzyl + H_2 → 2 toluene	−5.8	−8.2			−10.0 ± 0.4
rms error	3.1	1.1	0.7	1.0	

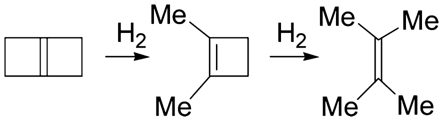
Table 8. Relative Enthalpies for Reaction of A, kcal/mol



reaction	CBS-QB3	G4	CBS-APNO
2 **A** → **B**	−56.0	−56.9	−57.2
B → **C**	−72.1	−71.4	
2 **A** → **C**	−128.1	−128.3	
C + 2H_2 → **D**	−63.8	−64.5	
D + 2H_2→ 2-cyclohexane	−36.9	−41.8	

using DFT. Even **C** has considerable strain associated with the repulsion between the two C═C bonds,[26] and the eclipsed methylene groups. This in turn leads to a large enthalpy of hydrogenation giving **D.** The hydrogenolysis energy of **D** is −42 kcal/mol as compared to two CH−CH bonds (−16 kcal/mol) leading to a strain energy of about 26 kcal/mol.

The remarkably large energy changes shown in Table 8 require some further consideration. An estimate of the strain energy of **A** might be obtained via consideration of the sequential hydrogenolysis of the cyclobutane CH_2−CH_2 bonds:



The CBS-APNO reaction enthalpies are −73.0 kcal/mol for the first step and −33.6 kcal/mol for the second (see the Supporting Information). The second step is calculated to be similar to that for the hydrogenolysis of cyclobutane (−37.0), whereas that for the first is 40 kcal/mol larger and might be attributed to the extra strain in **A** that would be distributed over the two rings. This must result in large measure from the difficulty in bending the relatively stiff C═C−Me bonds (135°) to the small angle in **A**. The total strain energy of **A** would then be about 40 plus that of the bicyclo[2.2.0]hexane ring (53 kcal/mol) giving a total of about 93 kcal/mol. It can also be estimated from the enthalpy of hydrogenation of **A** (61 kcal/mol, Table 5) and that of cyclobutene (33 kcal/mol) or 38 kcal/mol as the extra strain energy of **A**. Adding that of the parent ring gives about 91 kcal/mol in agreement with the above estimate.

The total strain energy for 2**A** is then about 184 kcal/mol. Since the dimerization of ethylene to form cyclobutane is exothermic by −19 kcal/mol, an estimate of the strain energy of **B** is roughly 184 less 19 and the energy for the conversion of **A** to **B** (57 kcal/mol) or about 108 kcal/mol. This is somewhat less to five times the strain in cyclobutane or 130 kcal/mol. The conversion of **B** to **C** is exothermic by −71 kcal/mol leading to an approximate strain energy for **C** of 108 − 71 or 36 kcal/mol.

The hydrogenation of **C** to give **D** is exothermic by −65 kcal/mol, and the reduction of two tetrasubstituted unstrained double bonds would be about 2 × 26 or 52 kcal/mol. The strain energy of **D** would then be 65−52 = 13 kcal/mol less than that of **C**, or about 23 kcal/mol. This is in agreement with the preceding estimate (26 kcal/mol) and seems to be a reasonable value for a compound having two chair cyclohexane rings. Although these are rough estimates and do not take into account possible changes in CH bond energies,[18] they do provide a way to understand the large energy changes for the set of reactions.

6. CALCULATIONS

All calculations were carried out using Gaussian-09.[27]

7. CONCLUSIONS

Enthalpies of hydrogenation are relatively easy to calculate with DFT and MP2 giving fairly good agreement with experiment, especially when large basis sets are used. The compound methods G4, CBS-APNO, and W1BD gave very good agreement. On the other hand, it is considerably more difficult to calculate the enthalpies of reduction of carbonyl compounds using DFT or MP2, and very large basis sets are needed. Again, G4, CBS-APNO, and W1BD gave quite satisfactory results.

The enthalpies of hydrogenolysis of C−C single bonds also were calculated, and these results were used in examining some small ring bicyclic hydrocarbons and propellanes. Calculations for the reactions of the highly strained bicyclo[2.2.0]hex(1,4)-ene and its derivatives provided information on the strain release in each step.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of calculated total energies for the several theoretical models along with the calculated energy changes for the reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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