

G2 ab Initio Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of C₃ Cyclic and Acyclic Ketones and Alcohols

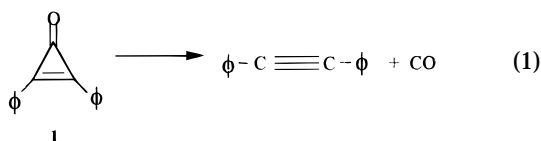
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We report the ab initio G2 enthalpies of hydrogenation and isomerization ($\Delta_{\text{hyd}}H$ and $\Delta_{\text{isom}}H$) in the gaseous state, at 298 K, of 8 C₃ cyclic and acyclic ketones and alcohols, including cyclopropenone, cyclopropenol, and allyl alcohol. $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ are found from the differences in total energy (E_0) of the participants in the hydrogenation and isomerization reactions. Combination of calculated $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ with one *experimental* enthalpy of formation (Δ_fH^{298}) in the set yields Δ_fH^{298} of all the rest. Results lead to an estimate of 20.5 kcal mol⁻¹ for the resonance energy of cyclopropenone.

Some time ago,¹ we obtained an experimental value for the enthalpy of formation (Δ_fH) of diphenylacetylene and we combined it with the photoacoustic calorimetric determination² of the enthalpy change for the reaction



to obtain Δ_fH of 2,3-diphenylcycloprop-2-en-1-one (**1**). When this Δ_fH is compared to a “resonance-free model”,³ one obtains 22 kcal mol⁻¹ as an estimate of the resonance energy of **1**. The interest in **1** stems from its structural relationship to cyclopropenone (**2**), the resonance energy of which has been of interest for many years.⁴ Experiments were carried out on **1** as a surrogate for **2**, which is not amenable to classical thermochemical experimentation.

More recently, accurate ab initio procedures have become available^{5,6} which permit calculation of the total energy (E_0) of small molecules to within ± 2 kcal mol⁻¹ or better.^{7,8} We have used the difference in E_0 between, for example, an alkene and an alkane to estimate the enthalpy of hydrogenation at 298 K in the gaseous state ($\Delta_{\text{hyd}}H^{298}$) of small, cyclic alkenes⁸



If the enthalpy of formation in the gaseous state at 298 K (Δ_fH^{298}) of either the alkene or the alkane is known, Δ_fH^{298} of the other follows

$$\Delta_{\text{hyd}}H^{298} = \Delta_fH^{298}(\text{alkane}) - \Delta_fH^{298}(\text{alkene}) \quad (3)$$

where $\Delta_fH^{298}(\text{H}_2) = 0$. The same method can be applied to enthalpies of isomerization in the gas phase at 298 K ($\Delta_{\text{isom}}H^{298}$). If a group of molecules is interconnected by hydrogenation and isomerization reactions, E_0 can be calculated for all of them, whence knowledge of Δ_fH^{298} for any one of them leads to Δ_fH^{298} of the rest. Infusion of empirical information into the ab initio calculation in this way improves agreement between calculated Δ_fH^{298} and experimental Δ_fH^{298} in those cases for which the experimental values are known. Estimated accuracy of the calculations for hydrocarbons is about 1.0 kcal mol⁻¹.

In this paper, we give E_0 , $\Delta_{\text{hyd}}H^{298}$, $\Delta_{\text{isom}}H^{298}$ and Δ_fH^{298} calculated by the G2 method for 8 3-carbon atom ketones and alcohols, we compare our results from computational thermochemistry with experimental results where they are available, and we discuss the resonance energy of **2** in the light of calculated and experimental Δ_fH^{298} values of several cyclopropenyl compounds.

Theoretical and Computational Methods

An overview of G2 and related calculations of $\Delta_{\text{hyd}}H^{298}$, $\Delta_{\text{isom}}H^{298}$ and Δ_fH^{298} of hydrocarbons has been given⁸ along with potential advantages of the method.^{8b} Original references give the theory in more detail.⁵

Briefly, the G2 method is a means of extrapolating from ab initio post-Hartree–Fock, Gaussian basis-set computations that are practical using contemporary computers to those that are not. Following geometry optimization at the MP2(full)/6-31G(d) level, calculated energies using 4 basis sets at 3 post-Hartree–Fock levels are used to estimate what the computed total energy E_0 of a molecule would be at the QCISD(T)/6-311+G(3d,2p) level. Computed zero-point energies are included in E_0 .

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Table 1. Calculated G2 Total Energies at 0 K (E_0) and Enthalpies at 298 K (H^{298}) of C_3 Ketones and Alcohols with Units in hartrees

| | E_0 | H^{298} |
|-----------------------------|-------------|-------------|
| hydrogen | -1.166 36 | -1.163 06 |
| cyclopropenone | -190.343 72 | -190.339 19 |
| cyclopropanone | -191.557 56 | -191.554 82 |
| propan-2-one (acetone) | -192.813 67 | -192.807 24 |
| cyclopropenol | -191.520 72 | -191.519 84 |
| cyclopropanol | -192.767 03 | -192.761 71 |
| propan-2-ol | -193.996 46 | -191.989 94 |
| propen-1-ol (allyl alcohol) | -192.775 78 | -192.769 69 |
| propan-1-ol | -193.989 39 | -193.982 77 |

Ab initio calculations described here were carried out using the program⁹ Gaussian 94, revision E.2. The more resource-intensive calculations were carried out at the National Center for Supercomputing Applications.

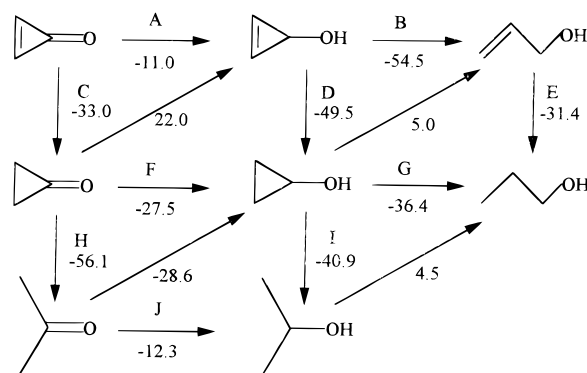
For isogyric reactions (those having the same number of α and β electron spins on the right and the left) the "HLC" correction of the G2 method drops out. Statistical thermodynamic corrections to E_0 , the total energy obtained by G2 calculations at 0 K, lead to H^{298} , the total enthalpy at 298 K, in the second column of Table 1. Translational and rotational enthalpies are classical ($^{3/2}RT$), and the electronic enthalpy is zero. Vibrational enthalpies are difficult to calculate and introduce some error into the enthalpy increment from E_0 to H^{298} . Fortunately, the error is a small part of a relatively small correction.¹⁰

Knowing H^{298} for a group of ketones and alcohols related to each other by hydrogenation or isomerization (along with H^{298} for hydrogen), we calculate $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ relating members of the group from differences in H^{298} for reactants and products in the hydrogenation or isomerization reaction. Alternatively, by an equivalent method, the ΔE_0 relating members of the set can be calculated and corrected from 0 to 298 K. We then select one of the values obtained by the G2 procedure, and from the experimental value of the enthalpy of formation, $\Delta_f H^{298}$ of the selected molecule, we calculate $\Delta_f H^{298}$ for all compounds in the set from $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ connecting the members of the set (see Figure 1).

Results and Discussion

E_0 and H^{298} values are given in Table 1 for two cyclic C_3 ketones, two cyclic alcohols, an acyclic ketone and three acyclic alcohols. Computed $\Delta_{\text{hyd}}H^{298}$ and $\Delta_{\text{isom}}H^{298}$ values are shown in Figure 1. The upward diagonal arrows represent enthalpies of isomerization. Numerous thermochemical cycles are evident which sum to zero as a check on the enthalpy changes shown.

Computed results for $\Delta_f H^{298}$ are given in Table 2 along with 5 experimental results from the literature. The value for acetone,¹¹ -52.23 ± 0.14 kcal mol⁻¹ was selected as the reference compound from which the remaining 7 $\Delta_f H^{298}$ values were calculated. The average deviation is about -1.0 kcal mol⁻¹, which is consistent with our results for hydrocarbons.⁸ The experimental result for

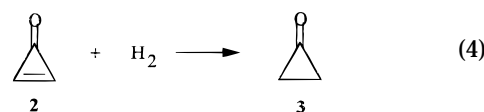
**Figure 1.** Calculated G2 enthalpies of hydrogenation and isomerization at 298 K of C_3 cyclic and acyclic ketones and alcohols. Diagonal arrows represent isomerizations. Units are kcal mol⁻¹.**Table 2. Calculated G2 and Experimental $\Delta_f H^{298}$ of C_3 Ketones and Alcohols in the gaseous state with Units in kcal mol⁻¹**

| | $\Delta_f H^{298}(\text{calc})$ | $\Delta_f H^{298}(\text{exp})$ | exp - calc |
|-----------------------------|---------------------------------|--------------------------------|------------|
| cyclopropenone | 36.9 | | |
| cyclopropanone | 3.9 | 3.8 ± 1.0^a | |
| propan-2-one (acetone) | -52.23 ± 0.14^b | -52.23 ± 0.14^b | |
| cyclopropenol | 25.9 | | |
| cyclopropanol | -23.6 | | |
| propan-2-ol | -64.5 | -65.20 ± 0.12 | -0.70 |
| propen-1-ol (allyl alcohol) | -28.6 | -29.76 ± 0.43 | -1.16 |
| propan-1-ol | -60.0 | -60.97 ± 0.12 | -0.97 |
| | arithmetic mean deviation (amd) | | -0.94 |

^a Found from appearance potentials (see ref 12). Not included in amd. ^b Selected $\Delta_f H^{298}$ (see ref 11).

cyclopropanone was not included in the mean deviation between experiment and calculation because of its large experimental uncertainty.¹² All three remaining experimental results are lower in energy than the calculated value; hence, the unsigned and signed average deviations are the same, indicating a systematic discrepancy. The average deviation could have been made to look "better" by selecting one of the alcohols as the enthalpic reference point, but given the stated accuracy goal of the G2 method as ± 2 kcal mol⁻¹ and the cancellation of errors on which the method depends, an "improvement" of a few tenths of a kcal mol⁻¹ would be largely cosmetic. Acetone was selected as the reference molecule because it is a ketone and the molecules of particular interest in what follows are cyclopropenone and cyclopropanone.

The computed $\Delta_{\text{hyd}}H^{298}$ for



is -33.0 kcal mol⁻¹, while that for cyclopropene¹³ is -53.5 kcal mol⁻¹. Taking cyclopropene as a "resonance free" model, one finds a resonance energy of 20.5 kcal mol⁻¹ for **2**. This compares favorably with the experimental

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(10) In the determination of ΔC_p of the hydrogenation of cyclopropanone to cyclopropanone for example, C_p of the ketones nearly cancel, leaving hydrogen as the only contributor to ΔC_p . See refs 8b,c for details.

(11) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447.

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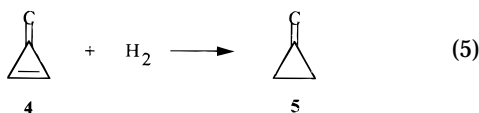
estimate of 22 kcal mol⁻¹ already cited for 2,3-diphenylcycloprop-2-en-1-one, the surrogate cycloalkenone **1** in reaction 1.

Alternatively, hydrogenation of cyclopropanone to cyclopropanol could have been used as a reference point for the resonance energy (yielding RE = 16.5 kcal mol⁻¹). This reference point has not been chosen because the change of inductive effect brought about by changing the oxygen atom to an OH group introduces an unnecessary complication.

Optimized MP2(full)/6-31G(d) geometries show that bond alternation is less in **2** than it is in bonds unstabilized by resonance. The double bond (135.2 pm) is longer than the double bond in ethene (133.9 pm),¹³ and the single bond in **2** (143.6 pm) is shorter than the ethane single bond (153.6 pm).¹³ The single and double bond lengths in cyclopropene of 130.3 and 150.7 pm have already been noted^{8a,b} in comparison with the experimental values¹⁴ of 129.6 and 150.9 pm. Further geometric data are available with the Supporting Information to this and related papers.⁸

The C=C bond length in **2** lengthens to a slightly stretched single bond of 156.7 pm in **3**, while the interior angle at the carbonyl carbon opens from 56.17 to 64.48°. The C=O bond length remains constant in **2** and **3** at 121.3 and 121.2 pm, respectively.

Methylene cyclopropene has a G2 computed value of -46 kcal mol⁻¹ for reaction 5, indicating about 8 kcal



mol⁻¹ stabilization of the endocyclic double bond by the exocyclic double bond, be it through resonance or strain alleviation at the trisubstituted carbon atom. The calculated endocyclic double bond length in **4** is 133.0 pm, longer than the exocyclic double bond (131.2 pm) and

(14) Stewart, J. J. S. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1 and references therein.

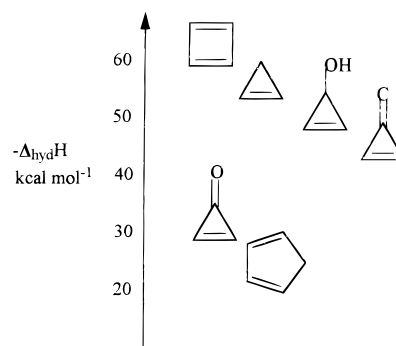
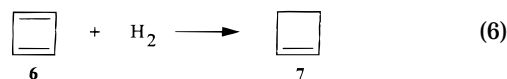


Figure 2. Enthalpy change $\Delta_{\text{hyd}}H^{298}$ (monohydrogenation) of several small-ring unsaturates.

shorter than the corresponding bond in **2**. The C-C single bonds in **4** are slightly longer than in **2** but shorter than those in cyclopropene. The interior angle at the methylene carbon is 55.20°. These geometric results are consistent with diminished resonance in **4** relative to **2**.

Antioaromatic cyclobutadiene^{8b}



has a computed $\Delta_{\text{hyd}}H^{298} = -63.3$ kcal mol⁻¹, and cyclopentadiene^{8c} has a G2 $\Delta_{\text{hyd}}H^{298}$ for monohydrogenation to cyclopentene of -23.5 kcal mol⁻¹.

The energetic pattern of monohydrogenations of several cyclopropenones, hydrocarbons, and cyclopropenyl alcohols treated in this work is summarized in Figure 2.

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Supporting Information Available: Tables of individual calculated gaussian energies and geometries (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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