Theoretical Calculation of Jet Fuel Thermochemistry.

1. Tetrahydrodicyclopentadiene (JP10) Thermochemistry Using the CBS-QB3 and G3(MP2)//B3LYP Methods

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Exo-THDCPD

\[ \Delta H^\circ(298.15K) \text{ (liquid)} = -126.4 \text{ kJ/mol} \]

High-level ab initio calculations have been performed on the exo and endo isomers of gas-phase tetrahydrodicyclopentadiene (THDCPD), a principal component of the jet fuel JP10, using the Gaussian G3 and G3(MP2) composite methods, as well as the CBS-QB3 method, and using a variety of isodesmic and homodesmotic reaction schemes. The impetus for this work is to help resolve large discrepancies existing between literature measurements of the formation enthalpy \( \Delta_H^\circ(298) \) for exo-THDCPD. We find that use of the isodesmic bond separation reaction \( C_{10}H_{16} + 14CH_4 \rightarrow 12C_2H_6 \) yields results for the exo isomer (JP10) in between the two experimentally accepted values, for the composite methods G3(MP2), G3(MP2)//B3LYP, and CBS-QB3. Application of this same isodesmic bond separation scheme to gas-phase adamantane yields a value for \( \Delta_H^\circ(298) \) within 5 kJ/mol of experiment. Isodesmic bond separation calculations for the endo isomer give a heat of formation in excellent agreement with the experimental measurement. Combining our calculated values for the gas-phase heat of formation with recent measurements of the heat of vaporization yields recommended values for \( \Delta_H^\circ(298) \) of -126.4 and -114.7 kJ/mol for the exo and endo isomers, respectively.

Introduction

The exo isomer of tetrahydrodicyclopentadiene (THDCPD) is the principal component of a synthetic liquid aircraft and missile fuel named JP10 that is also attractive for rocket applications because of its desirable physical properties and high energy density compared to more conventional, blended fuels. Production of JP10 involves Diels–Alder dimerization of cyclopentadiene to the endo dimer, followed by hydrogenation to endo-THDCPD (a solid at room temperature), and subsequent isomerization to the more stable (liquid) exo form. Despite many years of use in JP10, THDCPD has not been fully characterized thermochemically or spectroscopically. Schleyer and Donaldson studied the acid-catalyzed isomerization of the liquid and reported that at 100 °C in the presence of H_2SO_4 the composition of liquid THDCPD is 99% ± 0.6% exo isomer. This translates to an interconversion free energy \( \Delta G^\circ \) at 100 °C of approximately 14.4 kJ/mol, which should be close to the difference in gas-phase enthalpies at 298 K between the endo and exo isomers. In 1971, as part of their development of estimation techniques for strained molecules, Boyd et al. measured the vapor pressure, heat of vaporization, and heat of combustion of endo-THDCPD in the liquid phase. From their data they determined \( \Delta_H^\circ(298) = -60.2 \text{ kJ/mol} \) for the gas. Thermochemical data for exo-THDCPD in the liquid state is widely scattered, with reported values for \( \Delta_H^\circ(298) \) of -123, -134, and -159 kJ/mol.

This is an unacceptably large range for an experimentally derived value, and it calls for further investigation.

Recently, Chickos et al.\(^8\) used correlation gas chromatography to determine values of 49.1 and 50.2 kJ/mol for \(\Delta H_f^{(298)}\) of exo- and endo-THDCPD, respectively. Application of their value for \(\Delta H_f^{(298)}\) to the liquid heats of formation cited above yields heats of formation for gaseous exo-THDCPD of \(-74, -85, \) and \(-110 \) kJ/mol from refs 4, 6, and 7. Using the exo-endo \(\Delta H\) measured by Schleyer\(^9\) and these values for \(\Delta H_f^{(298)}\) of the gaseous exo isomer, one obtains estimates of \(-60, -71, \) and \(-96 \) kJ/mol for \(\Delta H_f^{(298)}\) of the gaseous endo isomer, from refs 4, 6, and 7. Note that while the first of these disparate values compares very well with Boyd’s direct measurement\(^3\) of \(-81\) kJ/mol, the second value of \(-71 \) kJ/mol should also be considered. On the basis of this exercise, one may conclude that the data reported in ref 7 is less likely to be correct than those in refs 4 and 6.

NASA is interested in obtaining accurate thermochemical data for liquid and gaseous exo-THDCPD to support the inhouse thermochemical and kinetic modeling of combustion processes and for inclusion in the NASA Glenn (formerly NASA Lewis) thermochemical database.\(^7\) This database currently contains accurate thermodynamic data for over 2000 compounds in the form of least-squares fits to \(C_p^{(T)}, H^\circ,\) and \(S^\circ \) versus \(T\). The database has been heavily used over the years by the aerodynamics community in conjunction with the NASA chemical equilibrium codes CEA and its predecessors,\(^7\) as well as several commercial packages. Hereinafter, all data used to generate the NASA coefficients have been obtained from published or experimental thermochemical and spectroscopic data\(^12\) or taken from standard compilations (JANAF, TPIS, TRC). Recent advancements in quantum chemical methods, particularly in composite methods utilizing density functional theory for geometries and vibrational frequencies, make it now possible to predict thermochemical data for small gas-phase molecules to high accuracy\(^13\) (4–10 kJ/mol), using reasonable computer resources. The large discrepancy alluded to above in the literature values for \(\Delta H_f^{(298)}\) of gaseous exo-THDCPD provides impetus to apply these methods to this molecule. With 10 heavy atoms, the \(C_{10}H_{16}\) molecules rank among the largest studied to date.

In this paper we assess several established composite methods for calculating the thermochemistry of several \(C_{10}H_{16}\) isomers: exo- and endo-THDCPD and adamantane, all similar

\[
C_{10}H_{16} + 14CH_4 \rightarrow 12C_2H_6
\]

(1) generate thermochemical information of accuracy sufficient for modeling kinetic breakdown pathways and for inclusion in the NASA Glenn database. We combine our calculated gas-phase heats of formation with published vaporization enthalpies\(^8\) to obtain reliable values for \(\Delta H_f^{(298)}\) of JP10 liquid. We recommend CBS-QB3 or G3(MP2)//B3LYP with the isodesmic bond separation scheme as the methods of choice for thermochemistry calculations. Part of our motivation for undertaking this study is to evaluate the use of well-established quantum chemical methods for obtaining accurate energetics for larger hydrocarbon molecules, including dimethyl tetrahydrodicylopentadiene, DMTTHDCPD (\(C_{12}H_{20}\), also known as the rocket fuel RJ4) and tricyclopentadiene (\(C_5H_{12}\)).

**Computational Details**

Standard ab initio molecular orbital calculations\(^20\) were performed with the Gaussian99\(^21\) and Gaussian03\(^22\) series of

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functions and $K_{CBS}$ model chemistry methods obtain more accurate results with the use of better basis set expansions. The complete basis set in ab initio calculations of electron correlation energies through economical recovery much of the truncation energy error in the calculations. To use this CBS approach, one equates the computed reaction enthalpy for one of the gaseous $C_{10}H_{16}$ isomers using, for example, the G3 method, one equates the computed reaction enthalpy for eq 1 using that quantum chemistry method ($\Delta H_f^{\text{ref}}(298) = 12H_{C_{10}H_{16}}^{G(298)} - 14H_{CH_4}^{G(298)}$) with the expression for $\Delta H_f^{\text{ref}}(298)$ computed from standard heats of formation and treating $\Delta H_f^{\text{ref}}(298)$ for the $C_{10}H_{16}$ isomer as an unknown. NIST Chemistry Webbook recommendations are used for the heats of formation of the reference species $CH_4(g)$ and $C_{10}H_{16}(g)$ (−74.9 ± 0.3 and −84.0 ± 0.3 kJ/mol, respectively). These values are derived from the work of Prosen and Rossini and Pittam and Pilcher, and have been adjusted to account for refinements in physical constants. A table of all the electronic energies, enthalpies, and thermal energy contributions (in Hartrees) computed for the $C_{10}H_{16}$ isomers used in the reaction schemes are provided as Supporting Information. Table 2 presents the results of the calculation of $\Delta H_f^{\text{ref}}(298)$ using the bond separation reaction calculated with the various methods, for different isotomers of $C_{10}H_{16}$. The results shown in Table 2 for adamantane show that use of the isodesmic bond separation reaction gives reasonably accurate heats of formation for all methods except G2, but especially good results are obtained using G3(MP2), G3(MP2)//B3LYP, and CBS-QB3. This gives us confidence in the results obtained for the isomeric THDCPD molecules. The $exo$-$endo$ and $exo$-adamantane energy differences in this table are direct comparisons of composite quantum chemistry energies for the different methods, i.e., no reaction scheme is involved. All methods give comparable results for these quantities. The values of the energy differences span less than 1 kJ for $endo$-$exo$ and less than 4 kJ/mol for $exo$-adamantane. The $exo$-$endo$ $\Delta H$ values are also consistent.

### Results and Discussion

To determine the standard enthalpy of formation for a gas-phase molecule, one must relate the electronic energy to a standard reference state. This is accomplished by using either the atomization energy or a reaction enthalphy where the

<table>
<thead>
<tr>
<th>method</th>
<th>G2</th>
<th>G2(MP2)</th>
<th>G3</th>
<th>G3(MP2)</th>
<th>G3(MP2) //B3LYP</th>
<th>CBS-QB3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAD</td>
<td>6.2</td>
<td>7.9</td>
<td>4.2</td>
<td>5.4</td>
<td>5.2</td>
<td>3.6</td>
</tr>
<tr>
<td>relative CPU time for adamantane</td>
<td>100</td>
<td>16.0</td>
<td>35.7</td>
<td>3.4</td>
<td>3.4</td>
<td>42.3</td>
</tr>
</tbody>
</table>

*CBS-QB3 results evaluated with the entire G2 test set.*

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with the experimentally determined estimate of 14.4 kJ/mol by Schleyer and Donaldson.\(^2\) Comparing the computed exo-adamantane and endo-endo \(\Delta H\) values with the experimental values (using the Boyd\(^3\) result for the endo isomer) suggests that the experimental value for exo-THDCPD of –74 kJ/mol from ref 4 is likely to be more accurate. The CBS and G\(x\) methods are sufficiently different in their approach, so the fact that they all give similar \(\Delta E\) values for the exo-endo isomerization is significant.

From Table 2, we can see for the adamantane molecule that the calculated heat of formation for the G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 methods are within 4 kJ/mol of experiment, well within the bounds of our desired accuracy. The G2 result for this molecule is the outlier with a 13.4 kJ/mol difference between calculation and experiment for \(\Delta H_f(298)\). The results for adamantane for these methods and the insensitivity of the \(\Delta H_f(298)\) values with the experimental derived values from the three theoretically derived values of enthalpy at 298 K and the standard \(\Delta H_f\) values for C(g) and H(g).

In the homodesmic reaction for adamantane, the number of secondary and tertiary carbon atoms are represented by \(n\)-propane and isobutane molecules on the right-hand side, and \(C_2H_6\) molecules are added to balance the equation:

\[
C_{10}H_{16}(g) \rightarrow 10C(g) + 16H(g) - \Delta H_{atom} (2)
\]

It can be seen from Table 3 that the atomization method yields somewhat larger errors for adamantane than does the bond separation reaction. The G2 atomization value is in excellent agreement with experiment, but the greater CPU time requirement for this method makes it impractical for thermochemical calculations of larger hydrocarbon molecules. Using the homodesmic reaction in eq 3 results in smaller absolute errors for G2, G2(MP2), and G3 and somewhat larger absolute errors for G3(MP2), G3(MP2)//B3LYP, and CBS-QB3. However, except for the G2(MP2) atomization value, all results for \(\Delta H_f(298)\) for adamantane computed using eqs 2 and 3 are within \(\pm 10\) kJ/mol of the recommended values of \(-134.4\) kJ/mol.

For the exo-THDCPD molecule, the isodesmic bond separation reaction and methods G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 yielded heats of formation spanning only 2.4 kJ/mol, from \(-78.8\) to \(-76.4\) kJ/mol. These results cause us to reject the experimental value of \(-110\) kJ/mol derived from ref 7. The values derived from refs 4 and 6, \(-85\) kJ/mol, and \(-85\) kJ/mol, are in better agreement with each other and with our calculated values. Of these two, however, our calculations agree better with the Smith and Good\(^4\) value of \(-74\) kJ/mol. Since the G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 methods give the best \(\Delta H_f(298)\) values for adamantane, we average their heats of formation for exo-THDCPD and get a preferred value of \(-77.3\) kJ/mol for the gas, which translates to \(-126.4\) kJ/mol for the liquid. The corresponding values for endo-THDCPD are \(-64.5\) kJ/mol for the gas and \(-114.7\) kJ/mol for the liquid.

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### Table 2. \(\Delta H_f(298)\) of C\(_{10}\)H\(_{16}\) (g) Isomers with the Isodesmic Bond Separation Reaction Using Various Quantum Chemical Methods (kJ/mol)

<table>
<thead>
<tr>
<th>Method</th>
<th>G2</th>
<th>G2(MP2)</th>
<th>G3</th>
<th>G3(MP2)</th>
<th>G3(MP2)//B3LYP</th>
<th>CBS-QB3</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>exo-THDCPD</td>
<td>–86.5</td>
<td>–82.9</td>
<td>–80.9</td>
<td>–76.4</td>
<td>–76.6</td>
<td>–78.8</td>
<td>–74.4, 85.6, 101,0</td>
</tr>
<tr>
<td>endo-THDCPD</td>
<td>–73.8</td>
<td>–70.2</td>
<td>–68.5</td>
<td>–64.1</td>
<td>–63.4</td>
<td>–66.0</td>
<td>–60.2, 51,6, 501,7</td>
</tr>
<tr>
<td>adamantane</td>
<td>12.7</td>
<td>12.7</td>
<td>12.4</td>
<td>12.2</td>
<td>12.6</td>
<td>12.8</td>
<td>14.3, 51,6, 501,7</td>
</tr>
<tr>
<td>adamantane (calcd – expt)</td>
<td>–13.4</td>
<td>–10.1</td>
<td>–8.7</td>
<td>–3.6</td>
<td>–1.2</td>
<td>–3.3</td>
<td></td>
</tr>
<tr>
<td>(\Delta H) (exo-adamantane)</td>
<td>61.3</td>
<td>61.6</td>
<td>62.2</td>
<td>61.6</td>
<td>59.0</td>
<td>58.9</td>
<td>60, 43, 30, 63, 30, 24, 730</td>
</tr>
</tbody>
</table>

### Table 3. \(\Delta H_f(298)\) of Adamantane by Atomization, Isodesmic and Homodesmotic Reactions Using Various Quantum Chemical Methods (kJ/mol)

<table>
<thead>
<tr>
<th>Method</th>
<th>G2</th>
<th>G2(MP2)</th>
<th>G3</th>
<th>G3(MP2)</th>
<th>G3(MP2)//B3LYP</th>
<th>CBS-QB3</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomization (eq 2)</td>
<td>–132.8</td>
<td>–124.0</td>
<td>–143.2</td>
<td>–142.7</td>
<td>–142.0</td>
<td>–126.9</td>
<td>–134.4</td>
</tr>
<tr>
<td>cale− expt (atomization)</td>
<td>1.4</td>
<td>10.4</td>
<td>–8.4</td>
<td>–8.3</td>
<td>–8.6</td>
<td>7.5</td>
<td>0.3</td>
</tr>
<tr>
<td>homodesmic (eq 3)</td>
<td>–141.1</td>
<td>–139.6</td>
<td>–143.5</td>
<td>–139.9</td>
<td>–138.8</td>
<td>–143.6</td>
<td>–134.4</td>
</tr>
<tr>
<td>cale− expt (homodesmic)</td>
<td>–6.7</td>
<td>–5.2</td>
<td>–9.1</td>
<td>–5.5</td>
<td>–4.4</td>
<td>–9.2</td>
<td></td>
</tr>
</tbody>
</table>

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To incorporate these results into the NASA Glenn thermochemical database, the enthalpy and entropy or free energy must be tabulated as a function of temperature from 200 to 6000 K. This is generally accomplished by computing these quantities and fitting the results to a series of polynomials. We used the G3(MP2)//B3LYP results because the geometries and normal mode vibration frequencies are computed using density functional theory (B3LYP) and are therefore presumed to be more accurate than the values determined by the other methods. Unscaled vibrational frequencies were used in computing the vibrational component of the molecular thermochemistry. CBS-QB3 also uses the B3LYP method for computing the molecular geometry and vibration frequencies, but it requires considerably more computational resources than G3(MP2)//B3LYP and is not practical for computing thermochemical properties of larger hydrocarbons. The Supporting Information contains the NASA Glenn polynomial coefficients for both isomers of hydrocarbons. The Supporting Information contains the practical for computing thermochemical properties of larger computational resources than G3(MP2)//B3LYP and is not.

For the exo isomer (JP-10), the isodesmic bond separation reaction and methods G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 yielded heats of formation spanning only 2.4 kJ/mol, from −76.4 to −78.8 kJ/mol. These results allow us to select the value of −74 kJ/mol derived from ref 4 as the best choice for ΔfH° of exo-THDCPD. Our choice is influenced by the very good agreement for ΔfH° of (isomeric) adamantane using the isodesmic bond separation reaction.

For the endo isomer, methods G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 with the isodesmic bond separation reaction yield heats of formation of −64.1, −63.4, and −66.0 kJ/mol, respectively, all clustered within 6 kJ/mol of the single experimental measurement of −60.2 kJ/mol. The excellent agreement with experiment for the endo isomer, and once again the very good agreement we obtained for ΔfH of the isomeric adamantane molecule gives us great confidence in the isodesmic bond separation reaction with G3-based methods and CBS-QB3.

Combining our best calculated values for the gas-phase heat of formation with recent measurements of the heat of vaporization yields recommended values for ΔfH°(298) of −126.4 and −114.7 kJ/mol for the exo and endo isomers, respectively.

Our success with these molecules gives us confidence that we can successfully study the rocket fuel dimethyl dicyclopentadiene, C_{12}H_{20}, also known as RJ4, and other larger potentially important hydrocarbons as candidates for high-performance fuels. Use of these methods in conjunction with the isodesmic bond separation scheme is now being carried out on RJ4.

**Supporting Information Available:** Molecular mass, molecular coordinates at equilibrium, principal axes, moments of inertia, rotational constants, unscaled vibrational frequencies, electronic energies, enthalpies, and thermal energy contributions (in Hartrees) computed for the C_{10}H_{16} isomers in the reaction schemes; NASA Glenn polynomial coefficients for both isomers of gaseous THDCPD; DHf data for reference compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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