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Theoretical Calculation of Jet Fuel Thermochemistry. 1. Tetrahydrodicylopentadiene (JP10) Thermochemistry Using the CBS-QB3 and G3(MP2)//B3LYP Methods

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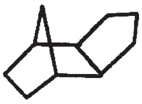

exo-THDCPD

$\Delta_f H^0$(298.15K) (liquid) = –126.4 kJ/mol^{-1}

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 G_x and $G_x(MP_x)$ 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 $\Delta_f H°(298)$ 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 $\Delta_f H°(298)$ 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 $\Delta_f H°(298)$liq of −126.4 and −114.7 kJ/mol for the *exo* and *endo* isomers, respectively.

Introduction

The *exo* isomer of tetrahydrodicylopentadiene (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.[1] 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[2] 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 $\Delta G°$ 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.[3] measured the vapor pressure, heat of vaporization, and heat of combustion of *endo*-THDCPD in the solid phase. From their data they determined $\Delta_f H°(298) = -60.2$ kJ/mol for the gas. Thermochemical data for *exo*-THDCPD in the liquid state is widely scattered, with reported values for $\Delta_f H°(298)$ of −123,[4,5] −134,[6] and −159 kJ/mol.[7]

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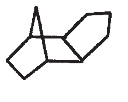
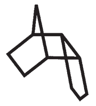
This is an unacceptably large range for an experimentally derived value, and it calls for further investigation.



exo-THDCPD (JP10)



endo-THDCPD

Recently, Chickos et al.[8] used correlation gas chromatography to determine values of 49.1 and 50.2 kJ/mol for $\Delta H^\circ_{\text{vap}}$(298) of *exo*- and *endo*-THDCPD, respectively. Application of their value for *exo* $\Delta H^\circ_{\text{vap}}$ 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* ΔH measured by Schleyer[2] and these values for $\Delta_f H^\circ(298)$ of the gaseous *exo* isomer, one obtains estimates of −60, −71, and −96 kJ/mol for $\Delta_f H^\circ(298)$ 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 −60.2 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 in-house thermochemical and kinetic modeling of combustion processes and for inclusion in the NASA Glenn (formerly NASA Lewis) thermochemical database.[9] This database currently contains accurate thermodynamic data for over 2000 compounds in the form of least-squares fits to C_p°, H°, and S° 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,[9−11] as well as in several commercial packages. Heretofore, 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 $\Delta_f H^\circ(298)$ 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 strained-ring compounds. For adamantane, which has well-characterized thermochemistry, we consider several well-known thermochemical formation reaction schemes using atomic and small-molecule precursors and assess them for their effectiveness in producing accurate heats of formation. We show that the G3(MP2),[14] G3(MP2)//B3LYP,[15] and CBS-QB3[16,17] quantum chemical ab initio methods, in combination with the isodesmic bond separation reaction,[18,19]

$$C_{10}H_{16} + 14CH_4 \rightarrow 12C_2H_6 \tag{1}$$

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 $\Delta_f H^\circ(298)$ 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, DMTHDCPD ($C_{12}H_{20}$, also known as the rocket fuel RJ4) and tricyclopentadiene ($C_{15}H_{18}$).

Computational Details

Standard ab initio molecular orbital calculations[20] were performed with the Gaussian98[21] and Gaussian03[22] series of

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TABLE 1. Comparison of Mean Absolute Deviation from Experiment for 299 Energies from the G2/97 Test Set (kJ/mol)

	method					
	G2	G2(MP2)	G3	G3(MP2)	G3(MP2) //B3LYP	CBS-QB3[a]
MAD	6.2	7.9	4.2	5.4	5.2	3.6
relative CPU time for adamantane	100	16.0	35.7	3.4	3.4	42.3

[a] CBS-QB3 results evaluated with the entire G2 test set.

programs. Energies were obtained at the G2,[23] G2(MP2),[24] G3,[25] and G3(MP2)[14] levels of theory and with two related methods, G3(MP2)//B3LYP[15] and CBS-QB3,[16,17] that utilize density functional theory with the Becke3LYP functional.[26,27]

All of these methods aim to approximate the combination of large atomic orbital basis set expansions and high-level electron correlation treatments, by using a series of well-tested[28] additivity approximations and an empirical term that is adjusted to obtain the best best overall agreement with experimental data for a large (299 molecule) test set of representative small molecules.

The cost of these calculations in computer resources (CPU time, disk space, memory) rises rapidly as the molecular size grows. For the large molecules we are concerned with in this study, there is significant motivation to decrease the CPU time requirement, which scales as N^K, where N is the number of basis functions and $K \approx 5-7$. The methods G2(MP2), G3(MP2), and G3(MP2)//B3LYP represent successive attempts to minimize required CPU time without significant loss in accuracy. In addition to the G*x* calculations, the complete basis set (CBS) model chemistry was evaluated for this system. CBS calculations economically recover much of the truncation energy error in ab initio calculations of electron correlation energies through the use of better basis set expansions. The complete basis set (CBS) model chemistry methods[16] obtain more accurate results in thermochemical calculations by the use of more accurate basis set expansions for determination of the electron correlation energies, molecular geometries, and fundamental vibration frequencies. In Table 1 are listed published values of the mean absolute deviation (MAD) from experiment for the energies of 299 molecules in the G2/97 test set calculated with methods G2, G2(MP2), G3, G3(MP2), G3(MP2)//B3LYP, and CBS-QB3. We evaluated these methods for *exo*- and *endo*-THDCPD molecules as well as for adamantane, isomeric to THDCPD, for which the thermochemistry is well characterized. Also included in Table 1 are relative timings for calculation of adamantane with these methods on a single CPU. From this table it is apparent that the G3 and CBS-QB3 methods yield the greatest overall accuracy, but at a high cost in CPU time, and that the G3(MP2) and G3(MP2)//B3LYP methods are the most economical. For somewhat smaller molecules, the relative CPU time for the CBS-QB3 method is only a factor of 2 greater than the G3(MP2) time and that method is favored for thermochemical computations.

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[29] or a reaction enthalpy where the standard formation enthalpies of all but one species are well-known. An attempt was made to standardize the reaction schemes through the use of so-called bond separation reactions,[18,19] isodesmic reactions where all formal bonds between non-hydrogen atoms are separated into the simplest parent (two heavy atom) molecules containing these same kinds of linkages. In 1997, a standard set of molecules whose heats of formation were known within 0.5 kJ/mol was defined as the parent molecule set for bond separation reactions and tested with G2 theory for a test set of 40 molecules.[19] This test yielded a mean absolute deviation from experiment that was a factor of 3 better than standard G2 theory using atomization energies for this test set.

In the present study, G2, G2(MP2), G3, G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 methods were used to determine the enthalpy of formation of *exo*-THDCPD, *endo*-THDCPD, and adamantane based on the isodesmic bond separation scheme (eq 1). To determine $\Delta_f H°(298)$ 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 ($\Delta H_{rxn}(298) = 12H_{C_2H_6}{}^{G3}(298) - H_{C_{10}H_{16}}{}^{G3}(298) - 14H_{CH_4}{}^{G3}(298)$) with the expression for $\Delta_f H°_{rxn}(298)$ computed from standard heats of formation and treating $\Delta_f H°(298)$ for the $C_{10}H_{16}$ isomer as an unknown. NIST Chemistry Webbook[30] recommendations are used for the heats of formation of the reference species CH_4(g) and C_2H_6(g) (-74.9 ± 0.3 and -84.0 ± 0.3 kJ/mol, respectively). These values are derived from the work of Prosen and Rossini[31] and Pittam and Pilcher,[32] respectively, 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 $\Delta_f H°(298)$ using the bond separation reaction calculated with the various methods, for different isomers 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* ΔH values are also consistent

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TABLE 2. $\Delta_f H°(298)$ **of** $C_{10}H_{16}$ **(g) Isomers with the Isodesmic Bond Separation Reaction Using Various Quantum Chemical Methods (kJ/mol)**

	G2	G2(MP2)	G3	G3(MP2)	G3(MP2) //B3LYP	CBS-QB3	expt
exo-THDCPD	−86.5	−82.9	−80.9	−76.4	−76.6	−78.8	−74,[4] −85,[6] −110[7]
endo-THDCPD	−73.8	−70.2	−68.5	−64.1	−63.4	−66.0	−60.2[3]
exo-endo ΔH	12.7	12.7	12.4	12.2	12.6	12.8	14,[3,4] 25[3,6] 50[3,7]
adamantane	−147.8	−144.5	−143.1	−138.0	−135.6	−137.7	−134.4 ± 2.3[30]
adamantane (calcd − expt)	−13.4	−10.1	−8.7	−3.6	−1.2	−3.3	
ΔH (*exo*-adamantane)	61.3	61.6	62.2	61.6	59.0	58.9	60,[4,30] 49,[6,30] 24[7,30]

TABLE 3. $\Delta_f H°(298)$ **of Adamantane by Atomization, Isodesmic and Homodesmotic Reactions Using Various Quantum Chemical Methods (kJ/mol)**

	G2	G2(MP2)	G3	G3(MP2)	G3(MP2) //B3LYP	CBS-QB3 (5d 7f)	expt
atomization (eq 2)	−132.8	−124.0	−142.8	−142.7	−142.0	−126.9	−134.4[30]
calcd − expt (atomization)	1.4	10.4	−8.4	−8.3	−8.6	7.5	
homodesmotic (eq 3)	−141.1	−139.6	−143.5	−139.9	−138.8	−143.6	−134.4[30]
calcd − expt (homodesmotic)	−6.7	−5.2	−9.1	−5.5	−4.4	−9.2	

with the experimentally determined estimate of 14.4 kJ/mol by Schleyer and Donaldson.[2] Comparing the computed *exo*-adamantane and *exo-endo* ΔH 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 ΔE 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 $\Delta_f H°(298)$. The results for adamantane for these methods and the insensitivity of the *exo*-adamantane and *endo-exo* energy differences give us confidence in our results obtained for the isomeric THDCPD molecules. For the *endo* isomer, methods G3(MP2), G3(MP2)//B3LYP, and CBS-QB3 using 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. This excellent agreement with experiment for the *endo* isomer joins the good agreement we obtained for the isomeric adamantane molecule, giving us confidence in the results of the isodesmic bond separation reaction. Schleyer and co-workers[33] estimated the strain energy in adamantane to be 24.3 kJ/mol. Using this value and the *exo*-THDCPD − adamantane energy difference, the strain energy in *exo*-THDCPD is estimated to be 85−90 kJ/mol. In these polycyclic molecules, the strain arises from the constraints imposed by the rings. Adamantane has less strain because it is based on cyclohexane rings instead of cyclopentane rings, and there is less deformation of the C−C−C bond angles.

In addition to the work reported for the isodesmic bond separation reaction, we evaluated the effectiveness of using the atomization reaction and a homodesmotic reaction for computing $\Delta_f H°(298)$ for adamantane. The results are shown in Table 3. The atomization reaction calculations used the protocol described in ref 29: atomization is defined as the total decomposition of a molecule to its constituent atoms in their ground electronic states, all species are in the gas phase at standard temperature and pressure, and the heat of atomization ΔH_{atom} derived from calculation is assumed to equal the experimental value. Therefore, for THDCPD, $\Delta_f H°$ can be determined as

$$C_{10}H_{16}(g) \rightarrow 10C(g) + 16H(g) - \Delta H_{\mathrm{atom}} \qquad (2)$$

Thus, for any given computational method, one obtains $\Delta_f H°$ for the $C_{10}H_{16}(g)$ isomers from the three theoretically derived values of enthalpy at 298 K and the standard $\Delta_f H°$ values for C(g) and H(g).

In the homodesmotic reaction for adamantine, 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:

$$C_{10}H_{16} + 12C_2H_6 \rightarrow 6C_3H_8 + 4HC(CH_3)_3 \qquad (3)$$

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 homodesmotic 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 $\Delta_f H°(298)$ for adamantane computed using eqs 2 and 3 are within ±10 kJ/mol of the recommended value[30] 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 t o−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, −74, 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 CBSQB3 methods give the best $\Delta_f H°(298)$ 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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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[34] and fitting the results to a series of polynomials.[35] 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[35] for both isomers of gaseous THDCPD, evaluated with the information gained from this study.

Conclusion

The results from this study allow us to make intelligent decisions for the heats of formation of the two isomers of tetrahydrodicyclopentadiene. We considered six ab initio computational methods with different levels of complexity and different approaches to finding the lowest energy for these large molecules. In addition we investigated several isodesmic and homodesmotic reaction schemes for the formation of THDCPD and its well-characterized isomer, adamantane. Our choices for the schemes to be investigated were guided by the rapidly evolving literature, with an important factor being NASA's need to use the recommended methods and reaction schemes for further work on fuel molecules larger than THDCPD. Thus, the primary criteria used for selection of a recommended method and reaction scheme are (1) the overall accuracy for calculating the $\Delta_f H$ of hydrocarbons, as described in the text, and listed in Table 1, (2) the value delivered for $\Delta_f H$ of adamantane, (3) agreement with the experimental value for the *endo* isomer of THDCPD, and (4) the possibility of its use for larger molecules.

One of the first conclusions of the study is that the G2 method is unsatisfactory for large molecules because the heat of formation it delivers for adamantane falls outside our desired range of chemical accuracy and it requires excessive computer resources when used on larger molecules.

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 $\Delta_f H°$ of *exo*-THDCPD. Our choice is influenced by the very good agreement for $\Delta_f H°$ 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 $\Delta_f H$ 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[8] yields recommended values for $\Delta_f H°$ (298)liq 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 dicylopentadiene, $C_{12}H_{20}$, 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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