

Thermochemistry of Benzvalene, Dihydrobenzvalene, and Cubane: A High-Level Computational Study

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Received: November 18, 1996; In Final Form: February 17, 1997[⊗]

The thermochemical properties of benzvalene, dihydrobenzvalene, and cubane were determined using *ab initio* molecular orbital calculations at the G2, G2(MP2), and G2(MP2,SVP) levels of theory. The enthalpy of formation, $\Delta_f H^\circ_{298}$, was examined with the use of homodesmotic and isodesmotic reactions. Based on the present theoretical calculations and available literature data, it is proposed that $\Delta_f H^\circ_{298} = 92 \pm 2$ kcal/mol for benzvalene and 55 ± 2 kcal/mol for dihydrobenzvalene. It is concluded that the discrepancy in the $\Delta_f H^\circ_{298}$ value of cubane, both experimentally and theoretically, warrants further experimental investigation. The heat capacity and entropy of benzvalene and dihydrobenzvalene were estimated on the basis of HF/6-31G(d) geometry and scaled harmonic frequencies. The adiabatic flame temperature was computed for each compound burning in air at 1 atm pressure using the estimated thermochemical data and compared with common hydrocarbon fuels. Consequently suitable surrogate fuels are identified for the characterization of global combustion processes of benzvalene, dihydrobenzvalene, cubane, and their derivatives.

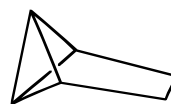
Introduction

A class of highly strained hydrocarbons have been proposed as potential high-energy density, liquid propellants.² Among them, benzvalene- and cubane-based compounds have received particular attention due to significant straining within their ring structures. The enhanced energy density manifests itself in their large enthalpies of formation compared to unstrained molecules. In addition, the thermal dissociation processes of these compounds are expected to be exothermic, which can yield local high temperatures ahead of the flame front to assist the liquid fuel vaporization process, a crucial step for achieving the desirable characteristics of rapid fuel–oxidizer mixing and combustion.

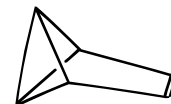
Successful understanding of the combustion characteristics of the highly energetic hydrocarbons is however hampered by the lack of accurate information on their thermochemical properties and the kinetic rates and mechanisms of reaction. In particular, while there are no experimental data reported for benzvalene and dihydrobenzvalene, only one direct measurement was reported³ for the enthalpy of formation ($\Delta_f H^\circ_{298}$) of cubane, yielding $\Delta_f H^\circ_{298} = 148.7 \pm 1.0$ kcal/mol. A more recent indirect measurement,⁴ based on the heat of combustion of 1,4-bis(methoxycarbonyl)cubane, has suggested a significantly larger $\Delta_f H^\circ_{298}$ value, at 159 kcal/mol. There have also been a number of theoretical studies for benzvalene,^{5,6} dihydrobenzvalene,⁶ and cubane.^{7–11} Among the predictions for cubane, it is noted that while Wiberg,⁸ Dailey,⁹ and Disch and Schulman¹⁰ were able to reproduce the $\Delta_f H^\circ_{298}$ value of 148.7 kcal/mol, others have generally predicted values lower by 10–15 kcal/mol than the experimental value.

In pursuing a converging estimate for the enthalpies of formation of these strained hydrocarbons to within the generally required ± 2 kcal/mol for reliable predictions of global and detailed combustion characteristics, we note that the recently developed G2 level of theory¹² and its variations^{13–15} have shown successes in predicting the atomization energies and other thermochemical data¹⁶ and have been used, for example, to predict $\Delta_f H^\circ_{298}$ for highly strained cyclobutadiene and tetrahe-

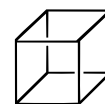
drane.¹⁷ In the present study, we have carried out *ab initio* MO calculations for benzvalene, dihydrobenzvalene, and cubane at the G2,¹² G2(MP2),¹³ and G2(MP2,SVP)¹⁴ levels. On the basis of the calculated total energies, we estimate $\Delta_f H^\circ_{298}$ values with the use of homodesmotic¹⁸ and isodesmotic¹⁹ reactions. The heat capacity and entropy were also obtained for benzvalene and dihydrobenzvalene from the vibrational frequencies computed at the HF/6-31G(d) level. The adiabatic flame temperatures were computed and compared with a number of exothermic fuels. On the basis of such comparisons, we recommend suitable surrogate fuels that can be used for initial studies of combustion characteristics of the strained hydrocarbons of interest to liquid propellant studies.



Benzvalene (1)



Dihydrobenzvalene (2)



Cubane (3)

Computational Methods

The *ab initio* MO calculations were carried out using the Gaussian 94 program.²⁰ Calculations were performed at the G2(MP2,SVP) level of theory¹⁴ for all three molecules. This level of theory corresponds to geometry optimization at the MP2(full)/6-31G(d) level, followed by energy calculations at the QCISD(T)/6-31G(d) level, with incorporation of zero-point energies, corrections due to basis set extension, and so-called higher order empirical corrections.¹² For benzvalene and dihydrobenzvalene, calculations were also performed at the G2-(MP2) level of theory,¹³ which corresponds to energy calculations at the QCISD(T)/6-311G(d,p)//MP2(full)/6-31G(d) level. To further verify the accuracy of the G2(MP2) and G2(MP2,-SVP) levels of theory in predicting enthalpies of formation of highly strained hydrocarbons, a full G2 calculation¹² was performed for benzvalene. It is noted that all three levels of theory correspond effectively to QCISD(T)/6-311+G(3df,2p) calculations with zero-point energy and higher level corrections and differ only in the additivity scheme of energy corrections.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

TABLE 1: Calculated G2, G2(MP2), and G2(MP2,SVP) Total Energies (hartrees), Enthalpies of Formation of Reference Species (kcal/mol), and Enthalpies of Homodesmic and Isodesmic Reactions at 0 K (kcal/mol)

| | G2 | G2(MP2) | G2(MP2,SVP) | $\Delta_f H^\circ_{298}^a$ | $\Delta_f H^\circ_0$ |
|-------------------------------------|-------------|-------------|-------------|----------------------------|----------------------|
| species | | | | | |
| benzvalene (1) | -231.666 77 | -231.662 65 | -231.663 67 | | |
| dihydrobenzvalene (2) | | -232.885 19 | -232.884 24 | | |
| cubane (3) | | | -308.848 00 | | |
| CH ₄ | -40.410 89 | -40.409 66 | -40.407 68 | -17.9 ± 0.1 ^b | -16.0 ^b |
| C ₂ H ₄ | -78.415 93 | -78.414 30 | -78.413 44 | 12.5 ± 0.1 ^b | 14.6 ^b |
| C ₂ H ₆ | -79.630 86 | -79.628 91 | -79.626 06 | -20.0 ± 0.1 | -16.3 ^c |
| C ₃ H ₆ | -117.645 08 | -117.642 57 | -117.641 04 | 4.8 ± 0.2 | 8.4 ^c |
| C ₃ H ₈ | -118.855 80 | -118.853 07 | -118.849 51 | -25.0 ± 0.1 | -19.8 ^c |
| (E)-2-C ₄ H ₈ | | -156.870 65 | | -2.7 ± 0.2 | |
| (Z)-2-C ₄ H ₈ | -156.871 89 | -156.868 53 | -156.866 36 | -1.7 ± 0.2 | 3.3 ^c |
| c-C ₄ H ₈ | | | -156.850 11 | 6.8 ± 0.2 | 13.0 ^c |
| n-C ₄ H ₁₀ | -158.081 17 | -158.077 64 | -158.073 39 | -30.2 ± 0.1 | -23.4 ^c |
| i-C ₄ H ₁₀ | -158.084 29 | -158.080 79 | -158.076 63 | -32.1 ± 0.2 | -25.2 ^c |
| reactions | | | | | |
| (1) | -80.7 | -80.9 | -80.9 | | |
| (2) | -95.8 | -96.7 | -96.8 | | |
| (3) | -35.3 | -36.0 | -34.7 | | |
| (4) | | -70.8 | -70.8 | | |
| (5) | | -71.0 | -71.0 | | |
| (6) | | -31.0 | -29.8 | | |
| (7) | | | -21.2 | | |
| (8) | | | -158.2 | | |
| (9) | | | -89.0 | | |

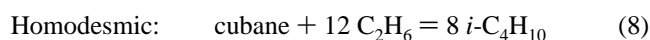
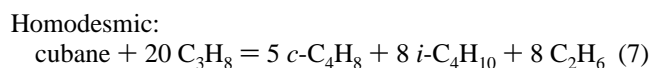
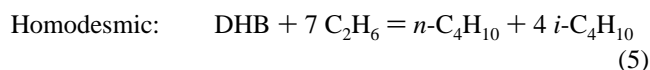
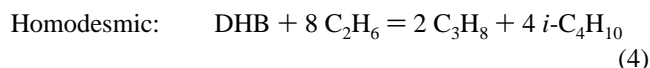
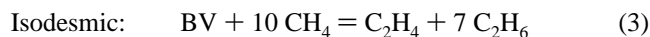
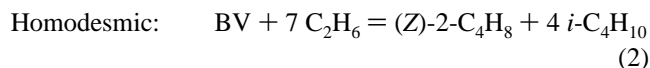
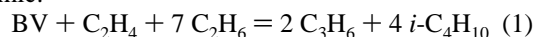
^a Unless otherwise indicated, the $\Delta_f H^\circ_{298}$ values are taken from Pedley et al.²⁵ ^b JANAF Table.²⁴ ^c Converted from $\Delta_f H^\circ_{298}$ and $H^\circ_{298} - H^\circ_0$ calculated with the HF/6-31G(d) harmonic frequencies, scaled by 0.8929.

Since past studies^{21–23} have confirmed the O_h symmetry of cubane, the geometry optimization was carried out assuming such a symmetry. For benzvalene and dihydrobenzvalene, no symmetry was assumed in geometry optimization. To obtain $\Delta_f H^\circ_{298}$ estimates, the sensible heat, $H^\circ_{298} - H^\circ_0$, was obtained with the harmonic frequencies calculated at the HF/6-31G(d) level, scaled by 0.8929, which is consistent with the zero-point energy calculation in the G2 scheme.

Results and Discussion

Enthalpy of Formation. To examine the consistency in the $\Delta_f H^\circ_{298}$ predictions, two homodesmic and one isodesmic reactions are assigned to each target species, i.e., benzvalene (BV), dihydrobenzvalene (DHB), and cubane. Hence, the following homodesmic and isodesmic reactions are considered:

Homodesmic:



While the isodesmic reactions are those with matching number of single, double, and triple C–C bonds in reactants and products,¹⁹ the homodesmic reactions require the further match of the number of C–H bonds of a given type in reactants and products.¹⁸ The experimental enthalpies of formation of the reference molecules are taken from the JANAF table²⁴ and from Pedley et al.²⁵ and are shown in Table 1.

We note that it is necessary to include multiple homodesmic and isodesmic reactions, because the designated reactions 1–9 involve large stoichiometric coefficients for the reference molecules, which then magnifies the uncertainties in the enthalpy of formation of these molecules. Take cubane as an example. Note that the uncertainty in the $\Delta_f H^\circ_{298}$ of the reference C₂H₆ molecule is ±0.1 kcal/mol. Such a small uncertainty, after multiplied by the stoichiometric coefficients of reactions 7, 8 and 9, becomes significantly larger. Specifically, if we use a $\Delta_f H^\circ_{298}$ value of -16.2 kcal/mol instead of -16.3 kcal/mol for C₂H₆, the enthalpy of formation of cubane would be 1.2 kcal/mol smaller from eq 8 and 1.2 kcal/mol larger from eq 9. The net difference of 2.4 kcal/mol is quite significant. Compounding the uncertainties in the $\Delta_f H^\circ_{298}$ values of all reference molecules, the resulting uncertainty could become very significant. Hence, by employing multiple homodesmic and isodesmic reactions for a single target molecule, the consistency of the $\Delta_f H^\circ_{298}$ prediction can also be examined, which then provides a relevant indication for the accuracy of $\Delta_f H^\circ_{298}$ estimates.

The computed energies at the three levels of the G2 methods are provided in Table 1. Although only the (Z)-2-C₄H₈ isomer is used in the homodesmic reaction 2, we have included its isomer, (E)-2-C₄H₈, in the calculation. At the G2(MP2) level, it was found that (Z)-2-C₄H₈ is less stable by 1.3 kcal/mol at 298 K than (E)-2-C₄H₈, in close agreement with the experimental value of 1.0 kcal/mol.^{25,26}

The total theoretical energies in Table 1 were then used to calculate the enthalpies of the homodesmic and isodesmic reactions 1–9, also shown in Table 1. The enthalpies of formation at 298 K were evaluated using the reaction enthalpies of Table 1 and the sensible heat $H^\circ_{298} - H^\circ_0$ based on HF/6-

TABLE 2: Enthalpies of Formation ($\Delta_f H^\circ_{298}$, kcal/mol) of Benzvalene, Dihydrobenzvalene, and Cubane

| species | present study | | | average ^a | literature |
|-------------------|---------------|---------|-------------|----------------------|--|
| | G2 | G2(MP2) | G2(MP2,SVP) | | |
| benzvalene | | | | 91.7 (0.4) | |
| homodesmic (1) | 92.0 | 92.2 | 92.2 | | 90.2, ^b 93.0 ^c |
| homodesmic (2) | 91.5 | 91.7 | 91.8 | | |
| isodesmic (3) | 91.4 | 92.1 | 90.8 | | |
| dihydrobenzvalene | | | | 54.6 (0.6) | |
| homodesmic (4) | | 54.8 | 54.8 | | 57.3 ^c |
| homodesmic (5) | | 54.9 | 54.9 | | |
| isodesmic (6) | | 54.6 | 53.4 | | |
| cubane | | | | 144.0 | 148.7 \pm 1.0, ^d 159 ^e |
| homodesmic (7) | | | 143.6 | | 139.8 ^f |
| homodesmic (8) | | | 145.6 | | 133.2, ^f 148.5 ^g |
| isodesmic (9) | | | 142.8 | | |

^a Averaged over corresponding values shown in columns 2–4. The value in parentheses is the standard deviation, which does not necessarily represent the uncertainties in the estimated $\Delta_f H^\circ_{298}$ (see text). ^b Reference 5, RMP2/6-31G(d)//HF/6-31G(d). ^c Reference 6, MP4/6-311G(d,p)//MP2/6-311G(d,p). ^d Experimental data, ref 3. ^e Indirect experimental data derived from the heat of combustion of 1,4-bis(methoxycarbonyl)cubane, ref 4. ^f Reference 7, HF/6-31G(d). ^g Reference 10, RMP2/6-31G(d)//HF/6-31G(d).

TABLE 3: Thermochemical Data of Benzvalene, Dihydrobenzvalene, and Cubane

| species | $\Delta_f H^\circ_{298}$ (kcal mol ⁻¹) | S°_{298} (cal mol ⁻¹ K ⁻¹) | $C_p(T)$, cal mol ⁻¹ K ⁻¹ | | | | | |
|---------|--|--|--|------|------|------|------|------|
| | | | 298 | 500 | 1000 | 1500 | 2000 | 2500 |
| BV | 92 | 66.8 | 19.9 | 34.4 | 51.3 | 58.3 | 61.9 | 63.6 |
| DHB | 55 | 68.8 | 21.3 | 37.7 | 58.7 | 67.7 | 72.2 | 74.5 |
| cubane | 148.7 | 64.4 | 23.9 | 45.5 | 69.6 | 79.2 | 83.9 | 86.2 |

31G(d) harmonic frequencies, scaled by 0.8929. The obtained results are presented in Table 2.

It is seen that for benzvalene the $\Delta_f H^\circ_{298}$ values estimated with all three levels of theory and with reactions 1–3 are consistent and are in close agreement. As such, they yield an average value of 91.7 kcal/mol with a 0.4 kcal/mol standard deviation. We note that the actual uncertainty in the estimated $\Delta_f H^\circ_{298}$ value should be larger than the standard deviation, because of the large multipliers for reference molecules and the uncertainties associated with their enthalpies of formation. For example, if a $\Delta_f H^\circ_0$ value of -15.9 kcal/mol was used for CH₄, we would obtain $\Delta_f H^\circ_{298}$ values that are 1 kcal/mol lower than those derived from isodesmic reaction 3, as shown in Table 2.

A comparison with the literature data in Table 2 shows that for benzvalene the present estimate is in good agreement with the reported theoretical values of Schulman and Disch⁵ and of Davis et al.⁶ On the basis of these results, we propose $\Delta_f H^\circ_{298} = 92 \pm 2$ kcal/mol for benzvalene, where the ± 2 kcal/mol uncertainty accounts mainly for the uncertainties in the $\Delta_f H^\circ_{298}$ values of the reference molecules in the homodesmic and isodesmic reactions.

The results obtained with benzvalene are encouraging considering that the G2(MP2,SVP) level presents a significant reduction in computational resources, while it basically produces the same result as the more resource-demanding G2(MP2) and G2 levels of theory. In the case of dihydrobenzvalene, calculations were performed at the G2(MP2) and G2(MP2,SVP) levels. The $\Delta_f H^\circ_{298}$ values obtained with reactions 4–6 are again consistent with each other, yielding an average of 54.6 kcal/mol with a 0.6 kcal/mol standard deviation. On the basis of the same consideration as for benzvalene, we propose a $\Delta_f H^\circ_{298}$ value of 55 ± 2 kcal/mol for dihydrobenzvalene. The result obtained by Davis et al.¹⁷ at the MP4/6-311G(d,p)//MP2/6-311G(d,p) level is somewhat larger.

For cubane, calculations at the G2 and G2(MP2) levels of theory are prohibitive because of excessive requirements for computational resources. Hence, calculations were performed only at the G2(MP2,SVP) level. The $\Delta_f H^\circ_{298}$ values obtained with reactions 7–9 differ by as much as 3.2 kcal/mol, as seen in Table 2. Such a difference is larger than those encountered

for benzvalene and dihydrobenzvalene and probably reflects increased cumulative error due to larger stoichiometric coefficients of the reference molecules in the corresponding homodesmic and isodesmic reactions. The average of the three values shown in Table 2 is 144.0 kcal/mol, which supports the lower experimental data of Kybett et al.³ The higher experimental value reported by Kirklin et al.⁴ appears to lie beyond the expected uncertainty with the level of theory employed in the present study. Regardless, the discrepancy in the cubane $\Delta_f H^\circ_{298}$ data shown in Table 2, both experimental and theoretical, warrants a redetermination of its enthalpy of formation.

Heat Capacity, Entropy, and Adiabatic Flame Temperature. The constant-pressure heat capacity and entropy are evaluated using the HF/6-31G(d) harmonic frequencies, scaled by 0.8929, for benzvalene and dihydrobenzvalene and the experimental vibrational frequencies²⁷ for cubane. The results are presented in Table 3. The complete thermochemical data in the form of the NASA polynomial²⁸ commonly used for combustion modeling can be obtained from the authors by request.

The adiabatic flame temperatures, T_{ad} , were computed with the thermochemical data just discussed for a fuel–air mixture at 1 atm pressure as a function of fuel equivalence ratio, as shown in Figure 1. For comparison, the adiabatic flame temperatures of acetylene, ethylene, propyne, and vinylacetylene are also shown in the same figure. It is seen that the T_{ad} values of benzvalene, dihydrobenzvalene, and cubane basically lie between that of ethylene, a moderately exothermic fuel, and that of acetylene, a strongly exothermic fuel. As expected, cubane–air mixtures attain the highest flame temperature among the three strained fuels, which is followed by benzvalene.

Studies on combustion characteristics often require a significant quantity of fuel for carrying out laboratory experiments. For the highly energetic fuels such as benzvalene and cubane, large quantities are often unavailable. Even if they are available, it is usually not safe to handle a large quantity of them. Hence, it is desirable to use suitable surrogate fuels of similar combustion characteristics. Because the adiabatic flame temperature is one of the most important parameters, which determines largely such combustion characteristics as the

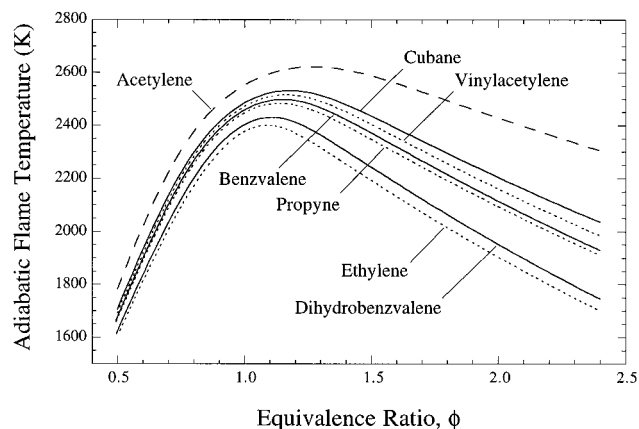


Figure 1. Comparison of adiabatic flame temperature plotted as a function of the equivalence ratio for fuel-air mixtures at 1 atm.

laminar burning velocity, and on the basis of comparison of the adiabatic flame temperatures of Figure 1, we suggest that the suitable surrogate fuels that would mimic the combustion energetics of dihydrobenzvalene, benzvalene, and cubane are respectively ethylene, propyne, and vinylacetylene.

Conclusions

High-level *ab initio* MO calculations were performed for energetic fuels including benzvalene, dihydrobenzvalene, and cubane. The enthalpies of formation were calculated with the use of homodesmic and isodesmic reactions. Based on present calculations and past literature data, it is proposed that $\Delta_f H^\circ_{298} = 92 \pm 2$ kcal/mol for benzvalene and 55 ± 2 kcal/mol for dihydrobenzvalene. The $\Delta_f H^\circ_{298}$ value calculated for cubane is somewhat lower than the experimental value of 148.7 kcal/mol. The discrepancy in $\Delta_f H^\circ_{298}$ values of cubane, both experimentally and theoretically, warrants further experimental investigation.

Acknowledgment. This research was supported by the Office of Naval Research under the technical monitoring of Dr. Gabriel Roy. The work utilized the computer system Power Challenge Array at the National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign.

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