



# Gas phase enthalpies of formation, isomerization, and disproportionation of mono- through tetra-substituted tetrahedranes: A G4(MP2)/G4 theoretical study

Sierra Rayne<sup>a,\*</sup>, Kaya Forest<sup>b</sup>

<sup>a</sup>Chemologica Research, Moose Jaw, Saskatchewan S6H 6M5, Canada

<sup>b</sup>Department of Environmental Engineering Technology, Saskatchewan Polytechnic, Moose Jaw, Saskatchewan S6H 4R4, Canada



## ARTICLE INFO

### Article history:

Received 28 September 2015

Received in revised form 2 November 2015

Accepted 7 November 2015

Available online 14 November 2015

### Keywords:

Tetrahedranes

1,3-Cyclobutadienes

Acetylenes

Enthalpy of formation

Isomerization

Disproportionation

## ABSTRACT

Gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ), enthalpies of disproportionation to two corresponding acetylene molecules ( $\Delta_{rxn} H^\circ_{(g),Td-acet}$ ), and enthalpies of isomerization from a tetrahedrane geometry to a 1,3-cyclobutadiene structure ( $\Delta_{isom} H^\circ_{(g),Td-CBD}$ ) were calculated for the mono- through tetra-substituted hydro, fluoro, chloro, bromo, methyl, ethynyl, and cyano carbon tetrahedrane derivatives at the G4(MP2) and G4 levels of theory. All derivatives have endothermic  $\Delta_f H^\circ_{(g)}$  indicative of the cage strain in these systems. In all cases,  $\Delta_{rxn} H^\circ_{(g),Td-acet}$  and  $\Delta_{isom} H^\circ_{(g),Td-CBD}$  are predicted to be substantially exothermic. High quality linear regression fits within a homologous series were obtained between the number of substituents and the G4(MP2)/G4 estimated  $\Delta_f H^\circ_{(g)}$ . Via calculations on lower homolog members, this strategy was employed to allow extrapolated G4 and/or G4(MP2)  $\Delta_f H^\circ_{(g)}$  (as well as some  $\Delta_{rxn} H^\circ_{(g),Td-acet}$  and  $\Delta_{isom} H^\circ_{(g),Td-CBD}$ ) to be obtained for the higher homolog t-butyl, trifluoromethyl, and trimethylsilyl carbon tetrahedrane derivatives.

© 2015 Elsevier B.V. All rights reserved.

Tetrahedrane (Fig. 1) has long captured the imagination of theoreticians and experimentalists [1]. Although synthesis of the parent carbon tetrahedrane has not yet been achieved, a number of its substituted derivatives have been prepared [2–10]. While much theoretical work has focused on the parent system (see, e.g., Refs. [11–23] and references therein), less computational effort has been undertaken on substituted tetrahedranes [24–32]. Continued theoretical interest in the tetrahedranes is important because advances in computing power and model chemistries (particularly composite methods) are facilitating increasingly accurate thermodynamic studies on these compounds. In concert, synthetic chemists are illustrating that the successful isolation of many tetrahedrane derivatives are likely within practical reach.

Our initial theoretical efforts focused on the mono- through tetra-substituted hydro (i.e., parent system), fluoro, chloro, bromo, methyl, ethynyl, and cyano carbon tetrahedrane derivatives. These substituents encompass a range of electron-withdrawing and releasing abilities and impart minimal conformational complexity. The G4 [33] and G4(MP2) [34] composite methods were employed using Gaussian 09 [35]. All calculations were conducted in the gas phase (1 atm) at 298.15 K. Geometries were visualized using

Gabedit v.2.2.12 [36] and Avogadro v.1.01 (<http://avogadro.openmolecules.net/>). Except where noted otherwise, all compounds converged absent imaginary frequencies.

Gas phase (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ) were calculated using the atomization approach [37–40] (Table 1). Prior work has established that G4(MP2)/G4 atomization  $\Delta_f H^\circ_{(g)}$  are expected to be at effective chemical accuracy [33,34,29,39–46]. None of these compounds have been synthesized; thus, no experimental  $\Delta_f H^\circ_{(g)}$  are available for comparison. Excellent agreement between the G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates was obtained, yielding a mean signed deviation (MSD) of 1.6 kJ/mol (G4-G4(MP2)), mean absolute deviation (MAD) of 3.3 kJ/mol, and a root mean squared deviation (RMSD) of 4.4 kJ/mol. Neither the G4(MP2) nor G4 methods converged on a tetrafluorotetrahedrane structure absent imaginary frequencies. Instead, both methods yielded a final geometry with two imaginary frequencies. A Gaussian-3 (G3) [47–49] calculation on this compound gave the desired tetrahedrane structure with no imaginary frequencies, and a corresponding atomization  $\Delta_f H^\circ_{(g)}$  at this level of 70.2 kJ/mol.

Linearly regressing the number of fluorine substituents ( $n = 1-3$ ) against the G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates provides high quality fits (G4(MP2):  $r^2 = 0.9994$ ,  $m = 516.7$ ,  $b = -114.6$ ; G4:  $r^2 = 0.9994$ ,  $m = 520.5$ ,  $b = -115.4$ ; values in kJ/mol). Extrapolating

\* Corresponding author. Tel.: +1 306 630 1422.

E-mail address: [sierra.rayne@alumni.ubc.ca](mailto:sierra.rayne@alumni.ubc.ca) (S. Rayne).

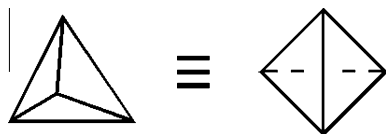


Fig. 1. Three- and two-dimensional representations of tetrahedrane.

Table 1

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ) using the atomization approach for various mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

Substituent	No.	G4(MP2)	G4
–H	tetra-	532.4	536.4
–CH <sub>3</sub>	mono-	498.0	501.0
–CH <sub>3</sub>	di-	464.5	466.2
–CH <sub>3</sub>	tri-	431.8	432.2
–CH <sub>3</sub>	tetra-	400.2	399.1
–C≡CH	mono-	769.9	772.9
–C≡CH	di-	1009.5	1011.3
–C≡CH	tri-	1250.2	1250.9
–C≡CH	tetra-	1490.9	1490.7
–C≡N	mono-	668.2	668.5
–C≡N	di-	821.5	818.4
–C≡N	tri-	988.4	982.1
–C≡N	tetra-	1166.1	1156.7
–F	mono-	403.7	406.7
–F	di-	284.2	286.4
–F	tri-	174.5	175.9
–F	tetra-	n/a <sup>a</sup>	n/a <sup>a</sup>
–Cl	mono-	529.7	535.2
–Cl	di-	529.0	535.9
–Cl	tri-	529.7	538.1
–Cl	tetra-	531.2	541.0
–Br	mono-	582.4	585.8
–Br	di-	632.9	635.2
–Br	tri-	683.2	684.3
–Br	tetra-	732.5	732.0

<sup>a</sup> Tetrahedrane structure converged with two imaginary frequencies.

these regressions to the  $n = 4$  (i.e., tetrafluoro-) member of the homologous series yields predicted G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates of 58.3 and 58.9 kJ/mol, respectively. In light of the higher atomization  $\Delta_f H^\circ_{(g)}$  predictive ability of the G4(MP2) and G4 methods versus the G3 level, and the high quality regression fits obtained over the mono- through trifluorinated range, we recommend the predicted G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates over the G3 atomization estimate. To ensure there are likely no discontinuities in the linear relationship between the number of fluorine substituents and the predicted G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  for the fluorinated tetrahedranes, we also conducted G3 calculations on the mono- through trifluorinated tetrahedranes, resulting in G3 atomization  $\Delta_f H^\circ_{(g)}$  estimates of 411.7 and 174.6 kJ/mol, respectively, for the mono- and tri-substituted derivatives (the difluorotetrahedrane would not converge at the G3 level despite several attempts). There is a high quality fit ( $r^2 = 0.9991$ ,  $m = -114.5$ ,  $b = 524.2$ ; values in kJ/mol) between the number of fluorine substituents and the G3 atomization  $\Delta_f H^\circ_{(g)}$  across the mono-, tri-, and tetra-fluorinated range, further suggesting the linear regression extrapolation of the  $n = 1-3$  G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  data to the  $n = 4$  homolog is valid.

With the exception of the chlorinated derivatives (for which there is negligible predicted variation in  $\Delta_f H^\circ_{(g)}$  with increasing chlorination), similarly strong linear regressions were obtained between the number of substituents and the G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates within each homologous series for the other tetrahedrane

derivatives (values in kJ/mol): methyl, G4(MP2) ( $r^2 = 0.998$ ,  $m = -32.6$ ,  $b = 530.2$ ), G4 ( $r^2 = 0.99990$ ,  $m = -34.0$ ,  $b = 534.5$ ); ethynyl, G4(MP2) ( $r^2 = 0.9999987$ ,  $m = 240.4$ ,  $b = 529.2$ ), G4 ( $r^2 = 0.9999981$ ,  $m = 239.3$ ,  $b = 533.2$ ); cyano, G4(MP2) ( $r^2 = 0.9989$ ,  $m = 166.1$ ,  $b = 495.9$ ), G4 ( $r^2 = 0.9988$ ,  $m = 162.8$ ,  $b = 499.4$ ); and bromo, G4(MP2) ( $r^2 = 0.99997$ ,  $m = 50.1$ ,  $b = 532.6$ ), G4 ( $r^2 = 0.99993$ ,  $m = 48.8$ ,  $b = 537.4$ ).

To determine if the G3 convergence on a tetrafluorotetrahedrane geometry with no imaginary frequencies was anomalous, a further suite of calculations at varying levels of theory was undertaken. The two closely spaced G4(MP2) and G4 imaginary frequencies for this compound occur at  $-69.8$  and  $-67.6$   $\text{cm}^{-1}$  and correspond to molecular vibrations that alternately elongate and compress adjacent carbons. If the imaginary frequencies are ignored, the calculated  $\Delta_f H^\circ_{(g)}$  are 69.0 (G4(MP2)) and 69.7 (G4) kJ/mol, or about 11 kJ/mol above the mono- through tri-fluorotetrahedrane regression predicted  $\Delta_f H^\circ_{(g)}$  for tetrafluorotetrahedrane at these two levels of theory. Slightly changing the bond angles and distances in the directions of the imaginary nodes and reoptimizing at these levels of theory leads to a cage-opened  $\text{C}_4\text{F}_4$  product  $\sim 200$  kJ/mol lower in free energy than the tetrahedrane structure and having a geometry analogous to the biradical-like species **6** found as a local minimum along the reaction coordinate for the conversion of the parent  $\text{C}_4\text{H}_4$  tetrahedrane to cyclobutadiene [50].

Additional geometry optimizations and corresponding frequency calculations were conducted using the M062X [51], PBE0D3 [52–56], B97D3 [57,55,56], B2PLYPD3 [58,55,56], and MP2 [59–63] methods each with the AUG-cc-pVTZ [64,65] and QZVP [66,67] basis sets, as well as calculations using the rest of the Gn methods (G1 [68], G2 [69], G2MP2 [70], G3MP2 [71], G3B3 [72], and G3MP2B3 [72]). With the converged G3 tetrafluorotetrahedrane geometry absent any imaginary frequencies used as the starting geometry, the G1, G2, G2MP2, and G3MP2 methods yielded a final cage-opened  $\text{C}_4\text{F}_4$  product as described above, while all other levels of theory considered gave a tetrafluorotetrahedrane geometry in return – except having two imaginary frequencies analogous to the G4(MP2) and G4 methods. Consequently, it appears unlikely that tetrafluorotetrahedrane is a minimum on the  $\text{C}_4\text{F}_4$  potential energy surface. While the G3 result is suggestive of a possible minimum, and thereby warrants a postulated  $\Delta_f H^\circ_{(g)}$  for tetrafluorotetrahedrane and consideration of its potential reactivity, the fact this method appears to stand alone in predicting the structure as a potential energy minima necessitates caution in the use of any associated data.

Increasing methyl and fluoro substitution is predicted to increase the thermodynamic stabilities of these substituted carbon tetrahedranes, versus increasing ethynyl, cyano, and bromo substitution decreasing the thermodynamic stability, and (as mentioned previously) no expected effect due to increasing chlorine substitution. All derivatives have endothermic  $\Delta_f H^\circ_{(g)}$  (ranging from about +60 to +1500 kJ/mol), indicative of the cage strain in these systems. Our G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  of 400.2/399.1 kJ/mol for tetramethyltetrahedrane is in modest agreement with the value of 429.7 kJ/mol reported by Balci et al. [25] at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) level using isodesmic reactions. A substantial number of prior theoretical works have estimated the  $\Delta_f H^\circ_{(g)}$  of the parent tetrahedrane at various levels of theory. This literature is summarized in Table 2, and our G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates for this compound are in excellent agreement with other high level calculations.

Tetrahedranes may disproportionate to two acetylenes, or may isomerize (Fig. 2) to a corresponding 1,3-cyclobutadiene. For each of the mono- through tetra-substituted carbon tetrahedrane derivatives discussed above, the enthalpies of these respective reactions were calculated at the G4(MP2) and G4 levels (Tables 3

Download English Version:

<https://daneshyari.com/en/article/5393014>

Download Persian Version:

<https://daneshyari.com/article/5393014>

[Daneshyari.com](https://daneshyari.com)