Gas phase bond dissociation enthalpies and enthalpies of isomerization/reaction for small hydrocarbon combustion related compounds between 300 and 1500 K: A comparison of Gaussian-4 (G4) theoretical values against experimental data

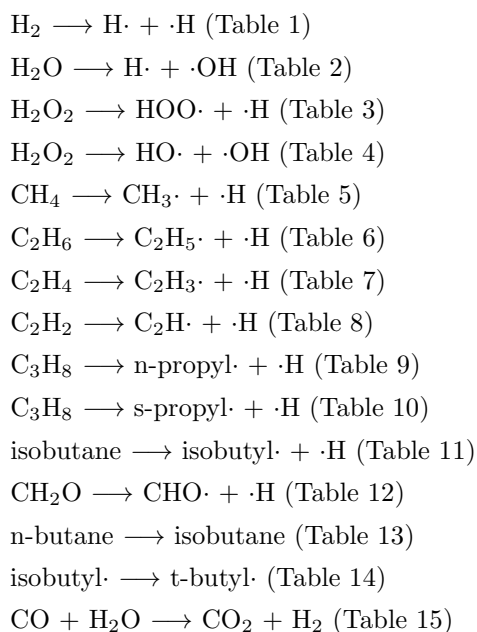Sierra Rayne [a] [*], Kaya Forest [b]

Keywords: bond dissociation enthalpy, isomerization enthalpy, enthalpy of reaction, hydrocarbon combustion modeling, gas phase, Gaussian-4 (G4), theoretical methods, benchmarking

Gas phase calculations at 1 atmosphere pressure between 300 and 1500 K at 200 K intervals were conducted using the Gaussian-4 (G4) composite method level of theory on a representative set of reactions having broad relevance in hydrocarbon combustion chemistry. Reasonable agreement between the experimental and theoretical data was obtained across the temperature range under consideration for all bond dissociation enthalpies, isomerization enthalpies, and enthalpies of reaction. For some reaction schemes, chemical accuracy for the theoretical method was maintained over the complete temperature range, whereas other systems displayed up to several kcal mol^{-1} deviations from experimental data. The direction of signed errors generally increased as the temperature was raised, and no general error trends were related to molecular size or reaction class.

Advanced modeling of combustion/pyrolysis processes and the thermal conversions of various materials requires detailed and accurate thermodynamic information for all relevant species at the temperatures of interest [1] [2] [3] [4]. The expense and difficulty of conducting thermally resolved experimental work, and recent improvements in the speed and accuracy of computational methods, have resulted in increased application of theoretical methods for studying these systems [5]. However, most experimental and theoretical work is conducted at standard temperatures (0 and 298.15 K). Further computational benchmarking efforts are needed at non-standard temperatures

and pressures on model systems in order to better constrain the abilities of theoretical methods.

To help address such issues, gas phase calculations at 1 atmosphere pressure between 300 and 1500 K at 200 K intervals were conducted using Gaussian 09 [6] with the G4 [7] composite method level of theory on the following set of reactions having broad relevance in hydrocarbon combustion chemistry:

$H_2 \longrightarrow H\cdot + \cdot H$ (Table 1)

$H_2O \longrightarrow H\cdot + \cdot OH$ (Table 2)

$H_2O_2 \longrightarrow HOO\cdot + \cdot H$ (Table 3)

$H_2O_2 \longrightarrow HO\cdot + \cdot OH$ (Table 4)

$CH_4 \longrightarrow CH_3\cdot + \cdot H$ (Table 5)

$C_2H_6 \longrightarrow C_2H_5\cdot + \cdot H$ (Table 6)

$C_2H_4 \longrightarrow C_2H_3\cdot + \cdot H$ (Table 7)

$C_2H_2 \longrightarrow C_2H\cdot + \cdot H$ (Table 8)

$C_3H_8 \longrightarrow$ n-propyl$\cdot + \cdot H$ (Table 9)

$C_3H_8 \longrightarrow$ s-propyl$\cdot + \cdot H$ (Table 10)

isobutane $\longrightarrow$ isobutyl$\cdot + \cdot H$ (Table 11)

$CH_2O \longrightarrow CHO\cdot + \cdot H$ (Table 12)

n-butane $\longrightarrow$ isobutane (Table 13)

isobutyl$\cdot \longrightarrow$ t-butyl$\cdot$ (Table 14)

$CO + H_2O \longrightarrow CO_2 + H_2$ (Table 15)

Reasonable agreement between the experimental and theoretical data was obtained across the temperature range under consideration for all bond dissociation enthalpies (BDEs; Tables 1-12), isomerization enthalpies ($\Delta_{isom}H$; Tables 13-14), and enthalpies of reaction ($\Delta_{rxn}H$; Table 15). For several reaction schemes (e.g., $H_2 \longrightarrow H\cdot + \cdot H$; $CH_4 \longrightarrow CH_3\cdot + \cdot H$; $C_3H_8 \longrightarrow$ n-propyl$\cdot + \cdot H$; isobutane $\longrightarrow$ isobutyl$\cdot + \cdot H$; $CH_2O \longrightarrow CHO\cdot + \cdot H$), chemical accuracy ($\leq$

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Table 1: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $H_2 \longrightarrow H\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T (K)	expt. [8] BDE (kcal mol^{-1})	G4 BDE (kcal mol^{-1})
300	104.2	104.5 [0.3]
500	104.8	105.1 [0.3]
700	105.4	105.7 [0.4]
900	106.0	106.3 [0.4]
1100	106.5	106.9 [0.4]
1300	107.0	107.4 [0.4]
1500	107.5	107.9 [0.5]

Table 2: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $H_2O \longrightarrow H\cdot + \cdot OH$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T (K)	expt. [8] BDE (kcal mol^{-1})	G4 BDE (kcal mol^{-1})
300	119.3	118.1 [-1.2]
500	120.1	118.9 [-1.2]
700	120.8	119.6 [-1.2]
900	121.4	120.1 [-1.2]
1100	121.8	120.6 [-1.2]
1300	122.3	121.1 [-1.2]
1500	122.6	121.4 [-1.2]

1 kcal mol^{-1} deviation from experimental data) was maintained over the complete temperature range.

With the exception of the BDE for ethyne ($C_2H_2 \longrightarrow C_2H\cdot + \cdot H$; Table 8) and the water gas shift reaction ($CO + H_2O \longrightarrow CO_2 + H_2$; Table 15), the direction of signed errors generally increased as the temperature was raised. There are no general error trends related to molecular size or reaction class, and some smaller systems (e.g., $H_2O_2 \longrightarrow HO\cdot + \cdot OH$; $C_2H_4 \longrightarrow C_2H_3\cdot + \cdot H$; $C_2H_2 \longrightarrow C_2H\cdot + \cdot H$) exhibited deviations on the order of several kcal mol^{-1}, even at room temperature. As such, the accuracy of the experimental and/or theoretical data as a function of temperature needs to be assessed on a case-by-case basis.

Acknowledgements

Table 3: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $H_2O_2 \longrightarrow HOO\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T (K)	expt. [8] BDE (kcal mol^{-1})	G4 BDE (kcal mol^{-1})
300	87.1	86.4 [-0.8]
500	87.6	87.2 [-0.4]
700	87.9	88.0 [0.1]
900	88.2	88.7 [0.5]
1100	88.5	89.3 [0.8]
1300	88.7	89.9 [1.2]
1500	88.9	90.4 [1.5]

Table 4: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $H_2O_2 \longrightarrow HO\cdot + \cdot OH$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T (K)	expt. [8] BDE (kcal mol^{-1})	G4 BDE (kcal mol^{-1})
300	51.4	48.6 [-2.8]
500	51.9	49.5 [-2.5]
700	52.1	50.0 [-2.1]
900	52.1	50.5 [-1.7]
1100	52.0	50.7 [-1.3]
1300	51.9	51.0 [-1.0]
1500	51.8	51.1 [-0.7]

Table 5: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $CH_4 \longrightarrow CH_3\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T (K)	expt. [8] BDE (kcal mol^{-1})	G4 BDE (kcal mol^{-1})
300	104.8	104.5 [-0.3]
500	105.9	105.6 [-0.3]
700	106.7	106.5 [-0.2]
900	107.3	107.0 [-0.2]
1100	107.6	107.5 [-0.2]
1300	107.9	107.7 [-0.2]
1500	108.0	107.9 [-0.1]

Table 6: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $C_2H_6 \longrightarrow C_2H_5\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [8] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	100.5	100.7 [0.2]
500	101.3	101.8 [0.4]
700	101.9	102.6 [0.6]
900	102.3	103.2 [0.8]
1100	102.6	103.5 [0.9]
1300	102.8	103.8 [1.0]
1500	102.9	104.0 [1.1]

Table 7: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $C_2H_4 \longrightarrow C_2H_3\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [8] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	108.0	110.0 [2.0]
500	108.8	110.9 [2.1]
700	109.3	111.6 [2.3]
900	109.7	112.1 [2.4]
1100	110.0	112.5 [2.5]
1300	110.1	112.7 [2.6]
1500	110.1	112.9 [2.7]

Table 8: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $C_2H_2 \longrightarrow C_2H\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [8] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	125.6	131.6 [5.9]
500	126.1	131.5 [5.4]
700	126.5	131.2 [4.8]
900	126.7	130.8 [4.1]
1100	126.9	130.3 [3.3]
1300	127.0	129.6 [2.6]
1500	127.0	128.9 [1.9]

Table 9: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $C_3H_8 \longrightarrow$ n-propyl$\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [9] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	101.0	100.7 [-0.3]
500	101.6	101.8 [0.1]
700	102.3	102.6 [0.2]
900	102.7	103.1 [0.5]
1100	102.9	103.5 [0.6]
1300	103.1	103.8 [0.7]
1500	103.2	104.0 [0.8]

Table 10: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $C_3H_8 \longrightarrow$ s-propyl$\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [9] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	99.2	97.9 [-1.4]
500	99.7	98.9 [-0.9]
700	100.0	99.6 [-0.4]
900	100.2	100.2 [-0.1]
1100	100.3	100.5 [0.2]
1300	100.4	100.8 [0.4]
1500	100.4	101.0 [0.6]

Table 11: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction isobutane $\longrightarrow$ isobutyl$\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

T	expt. [10] BDE	G4 BDE
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	100.9	100.8 [-0.1]
500	101.6	101.8 [0.2]
700	102.2	102.6 [0.4]
900	102.5	103.2 [0.7]
1100	102.8	103.6 [0.8]
1300	102.9	103.9 [1.0]
1500	103.1	104.0 [0.9]

Table 12: Experimental and G4 calculated gas phase bond dissociation enthalpies (BDE) at 1 atmosphere for the reaction $CH_2O \longrightarrow CHO\cdot + \cdot H$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

| T | expt. [8] BDE | G4 BDE |
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	88.7	88.2 [-0.5]
500	89.6	89.0 [-0.5]
700	90.2	89.7 [-0.5]
900	90.6	90.2 [-0.4]
1100	90.9	90.5 [-0.4]
1300	91.1	90.7 [-0.3]
1500	91.1	90.9 [-0.3]

Table 13: Experimental and G4 calculated gas phase isomerization enthalpy ($\Delta_{isom}H$) at 1 atmosphere for the reaction n-butane $\longrightarrow$ isobutane between 300 and 1500 K. Values in brackets represent deviations from experimental data.

| T | expt. [10] [11] BDE | G4 BDE |
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	-2.1	-2.0 [0.1]
500	-2.1	-1.9 [0.2]
700	-2.0	-1.8 [0.2]
900	-2.1	-1.8 [0.3]
1100	-2.3	-1.7 [0.6]
1300	-2.4	-1.7 [0.7]
1500	-2.9	-1.7 [1.2]

Table 14: Experimental and G4 calculated gas phase isomerization enthalpy ($\Delta_{isom}H$) at 1 atmosphere for the reaction isobutyl$\cdot \longrightarrow$ t-butyl$\cdot$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

| T | expt. [10] BDE | G4 BDE |
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	-4.2	-4.8 [-0.6]
500	-5.0	-4.9 [0.1]
700	-5.8	-5.1 [0.7]
900	-6.2	-5.1 [1.1]
1100	-6.6	-5.2 [1.4]
1300	-6.8	-5.2 [1.6]
1500	-7.1	-5.2 [1.9]

Table 15: Experimental and G4 calculated gas phase reaction enthalpy ($\Delta_{rxn}H$) at 1 atmosphere for the reaction $CO + H_2O \longrightarrow CO_2 + H_2$ between 300 and 1500 K. Values in brackets represent deviations from experimental data.

| T | expt. [8] BDE | G4 BDE |
(K)	(kcal mol^{-1})	(kcal mol^{-1})
300	-9.8	-11.3 [-1.5]
500	-9.5	-11.0 [-1.5]
700	-9.0	-10.7 [-1.6]
900	-8.5	-10.4 [-1.8]
1100	-8.1	-10.0 [-2.0]
1300	-7.6	-9.8 [-2.2]
1500	-7.2	-9.6 [-2.3]

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