Computational Study of Heats of Formation and Combustion of Hydrocarbons

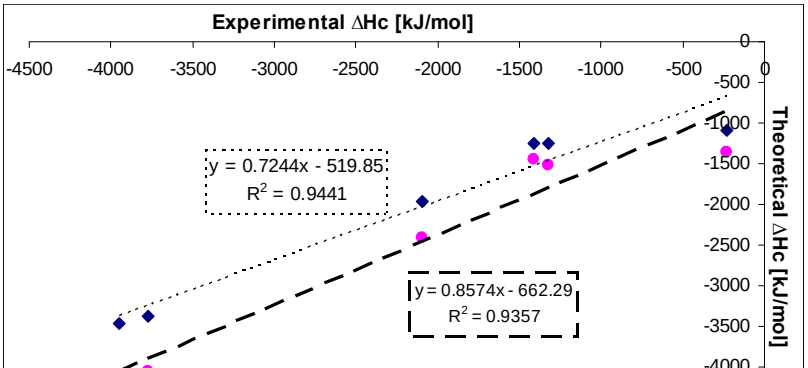
Results

Computational study of CO_2 yielded a bond angle of 180.000° and a bond length on either side of 1.189A° for both theories. The vibrational frequencies ranged from 510.9975-2565.4229cm^{-1}in AM1 theory and 507.4645-2386.6867cm^{-1}in PM3 theory. For O_2 the bond length was 1.086A° in AM1 theory and 1.170A° in PM3 theory. The vibrational frequency was 2091.9282 cm^{-1}in AM1 theory and 2096.9159 cm^{-1}in PM3 theory. The optimizations of water gave a bond angle of 105.532° in AM1 and 105.532° in PM3. The bond length was 0.961A° in both theories. The vibrational frequencies ranged from 1884.6692-3583.4064cm^{-1} in both AMI and PM3 theories.

The combustion equation for each hydrocarbon was used to solve for the heat of combustion of each molecule using the standard enthalpies of formation for CO_2, water and O_2. Both the optimized and the standard experimental NIST values were used during this process and the results can be seen in Figure 1. The results from the entire class were compiled for a variety of hydrocarbons and the results can be seen in Appendix 1. Comparison of the accuracy of the two theories was done graphically as seen in Figure 2.

					AM1				PM3			
Molecule	**Molecular Weight**	**Experimental ΔfH° [kJ/mol] (from NIST)**	**Experimental ΔHc [kJ/mol]**	**Experimental ΔHc [kJ/gram]**	**Theoretical ΔfH° [Hartree] (From Web MO)**	**Theoretical ΔfH° [kJ/mol] (From Web MO)**	**Theoretical ΔHc [kJ/mol]**	**Theoretical ΔHc [kJ/gram]**	**Theoretical ΔfH° [Hartree] (From Web MO)**	**Theoretical ΔfH° [kJ/mol] (From Web MO)**	**Theoretical ΔHc [kJ/mol]**	**Theoretical ΔHc [kJ/gram]**
Ethylene (C2H4)	28.054	52.4	-1323.06	-47.16	0.081124	212.991	-1242.03	-44.27	0.081124	212.991	-1510.48	-53.84
Toluene (C7H8)	92.141	50	-3771.82	-40.94	0.155268	407.656	-3371.94	-36.60	0.155268	407.656	-4052.76	-43.98
Ethyl Acetate (C4H8O2)	88.106	-445.43	-2095.89	-23.79	-0.026798	-70.358	-1963.62	-22.29	-0.030468	-79.994	-2416.96	-27.43
Acetylene (C2H2)	26.038	227	-1255.83	-48.23	0.096792	254.127	-1086.78	-41.74	0.112238	294.681	-1358.82	-52.19
CO2		-393.5			-0.111994	-294.040			-0.120877	-317.363		
H2O		-241.83			-0.070210	-184.336			-0.070210	-184.336		
O2		0			0.009177	24.094			0.037338	98.031		

Figure 1: Results from molecular modeling done on WebMO. Modeling was done to obtain the formation enthalpies of each hydrocarbon as well as water, oxygen and carbon dioxide. The heats of combustion were then calculated using Hess' Law and through proper stoichiometric adjustment of the general combustion equation: Hydrocarbon + O_2 → CO_2 + water. The per gram equivalents were found by dividing by the molar mass.



Discussion

This computational study yielded results that were quite useful. In estimating the vibrational frequencies and bond angles, both theories provided reasonable results and there was no stark difference between the two theories. Both theories estimated the C-O bond in CO_2 to be 1.189A°, in actuality; the bond length is 1.20A° (Brown, 2005). The O=O bond was estimated at 1.086A° by AM1 theory, and 1.170A° by PM3 theory. The actual bond length is supposed to be between 1.207-1.278A°(Brown, 2005). Both theories predicted a bond length of 0.961A° for the O-H bond in water, which is exactly the established value (Brown, 2005).

When it comes to predicting heats of combustion, AM1 theory tends to underestimate values, while PM3 tends to over estimate values. This is particularly true when you only consider the values molecules in Figure 1 as some discrepancies seem to arise when it comes to the larger class data in the Appendix data. Thus, a more accurate result might in some cases be determined by averaging the two values. Both theories also seem to provide better predictions when it comes to smaller and simpler molecules, though this is not always the case.

Studying the heats of combustion for various hydrocarbons has a useful application in today's world in that it is what people use to fuel their industrialized lives. The negative sign reflects that energy is being released in combustion while the absolute value of ΔH_c tells us how much is being released. Consider the topic of using fuels besides gasoline to power cars. Gasoline is mostly octane which releases between 50 to 60 kilojoules of energy per gram. One of the primary fuels being listed an alternative to gasoline is ethanol and many car makers have already outfitted their vehicles to run on it. These days it's a cheap, renewable

alternative to gasoline and solves much of the problems farmers have with regards to their crop surpluses. However, one might not be so quick to embrace it as a proper alternative when one considers that it only releases about half (20-30kJ/gram) the energy of gasoline when combusted! Thus, the higher ethanol content in a fuel will result in lower amount of energy available to power the engine. Now, it may also be worthy to investigate the efficiency of the engines our world uses as it might not be such a valid concern if engines are using less energy than what is available to them for combustion. For example, it all engines are only using 10kJ/gram of what is released, the fuel may become irrelevant.

As it stands, better fuels may be obtained through the combustion of bigger hydrocarbons. There is a general upward trend in the amount of energy released as the size of the hydrocarbon increases. For example, methane releases 50kJ/gram while decane releases 67kJ/gram.

Substituents also seem to have an effect, in particular the effects of alcohol groups which seem to decrease the amount of energy released during combustion. For example, butane releases between 30-40kJ/gram of energy during combustion while its alcohol counterpart, butanol, only yields 13-24 kJ/gram during combustion. The same trend can be observed when comparing propane(50-70kJ/gram) and propanol(34kJ/gram) as well as methane(50kJ/gram) and methanol(30-40kJ/mol).

Aromaticity also seems to play an important role and can be observed by comparing benzene (31-43kJ/gram) and hexane (68kJ/gram). It's also observable in the comparison of the energy released by naphthalene (39kJ/gram) and decane (67kJ/gram). Another interesting comparison is the shape/arrangement of the molecules. Anthracene and phenanthrene have the exact same molecular formula and both are composed of three aromatic rings. Yet phenanthrene releases significantly more energy (58-70kJ/gram) than anthracene (38kJ/gram). The only notable difference is that the structure of anthracene has the rings lined up in a row, while phenanthrene has the rings arranged in more of an arch-type shape. Somehow, this arrangement seems to store more energy in its bonds than the plain line of aromatic rings.

This experiment was useful in investigating what other techniques a chemist might find useful in obtaining certain data. It is certainly not a method that one would necessarily associate with chemistry but it is equally effective and valid. It allows us to find out a lot of information relatively easily and may be arguably quicker and cheaper than carrying out each individual combustion reaction. The data also yielded some interesting results on the effects

different types of molecules can have on the energy released during combustion. However, from all of the data presented, it seems that phenanthrene is the "winner" in the game of most efficient fuel. It is followed closely by kerosene, decane, hexane and octane. From these results it is reasonable to conclude that any large, bulky, unsubstituted hydrocarbon would make an excellent fuel.

References

Brown, William. Organic Chemistry. 4. Toronto, Canada: Brooks/Cole, 2005

McQuarrie, Donald. Physical Chemistry: A Molecular Approach. 1. Sausalito, CA, US: University Science Books, 1997.

Smith, Jonathan., Nienow, Amanda. "Computational Study of Heats of Formation and Combustion of Hydrocarbons." Gustavus Kinetics Lab Manual 1(2008): 1-4.

"*On my honor I pledge that I have not given, received, nor tolerated others' use of unauthorized aid in the completion of this work.*"

Appendix 1

Molecule	Experimental ΔHc [kJ/mol]	Experimental ΔHc [kJ/gram]	AM1 Theoretical ΔHc [kJ/mol]	AM1 Theoretical ΔHc [kJ/gram]	PM3 Theoretical ΔHc [kJ/mol]	PM3 Theoretical ΔHc [kJ/gram]
Methanol (CH3OH)	-1065.70	-33.26	-1177.73	-36.76	-1197.30	-37.37
Methanol (CH3OH)	-1065.70	-33.26	-1177.73	-36.76	-1197.30	-37.37
Methanol (CH3OH)	-1344.36	-41.96	-1083.21	-33.81	-1251.73	-39.07
Methanol (CH3OH)	-979.91	-30.58	-694.20	-21.67	-703.50	-21.96
Methane(CH4)	-802.67	-50.03	-800.65	-49.91	-900.56	-56.14
Ethylene (C2H4)	-1323.06	-47.16	-1242.03	-44.27	-1510.48	-53.84
Ethylene (C2H4)	-1410.98	-50.30	-1242.03	-44.28	-1451.90	-51.76
Ethylene (C2H4)	-1323.17	-47.17	-1483.90	-52.90	-1481.28	-52.80
Ethylene (C2H4)	-1323.17	-47.17	-1483.90	-52.90	-1481.28	-52.80
Ethylene (C2H4)	-1323.10	-47.16	-1339.40	-47.74	-1340.10	-47.77
Ethylene (C2H4)	-1411.00	-50.20	-1241.00	-44.20	-1402.00	-49.90
Ethanol (C2H6O)	-1391.51	-30.21	-1186.82	-25.76	-1428.66	-31.01
Ethanol (C2H6O)	-1036.70	-26.77	-1249.38	-27.12	-1233.23	-22.50
Ethanol (C2H6O)	-1036.70	-22.50	-1233.23	-26.77	-1249.38	-27.12
Ethanol (C2H6O)	-1278.40	-27.75	-1253.20	-27.20	-1276.20	-27.70
Ethanol (C2H6O)	-1278.50	-27.80	-1097.40	-23.80	-1071.70	-23.30
Ethanol (C2H6O)	-1410.00	-30.60	-1173.00	-25.40	-1302.00	-28.20
Ethanol (C2H6O)	-1278.50	-27.76	-1169.94	-25.40	-1374.24	-29.84
Acetylene (C2H2)	-227.00	-48.23	-1086.78	-41.74	-1358.82	-52.19
Propane (C3H8)	-3068.93	-69.60	-2255.34	-69.60	-2396.95	-54.36
Propane (C3H8)	-2043.15	-46.30	-2051.57	-46.52	-2055.19	-46.60
Propene (C3H6)	-2531.23	-60.12	-2232.62	-53.03	-2108.39	-50.08
2-Propanol (C3H8O)	-2510.39	-33.87	-2320.23	-31.30	-2716.84	-36.65
Acetic Acid (CH3COOH)	-837.70	-13.95	-721.70	-12.02	-916.73	-15.27

Molecule	Experimental ΔHc [kJ/mol]	Experimental ΔHc [kJ/gram]	AM1 Theoretical ΔHc [kJ/mol]	AM1 Theoretical ΔHc [kJ/gram]	PM3 Theoretical ΔHc [kJ/mol]	PM3 Theoretical ΔHc [kJ/gram]
Butane (C4H10)	-2657.19	-45.73	-2658.09	-45.73	-2667.73	-45.90
Butane (C4H10)	-2506.19	-33.87	-2304.42	-31.14	2729.18	-36.88
Butane (C4H10)	-2506.19	-33.81	-2304.41	-31.09	-2729.53	-36.83
Butanol (C4H9OH)	-993.20	-13.40	-1332.71	-17.98	-1361.38	-18.37
Butanol (C4H9OH)	-993.20	-13.40	-1332.71	-17.98	-1361.38	-18.37
Ethyl Acetate (C4H8O2)	-2095.89	-23.79	-1963.62	-22.29	-2416.96	-27.43
2-methyl-butane (C5H12)	-3909.15	-54.18	-3043.80	-42.19	-3161.93	-43.83
Pentanol (C5H12O)	-4977.62	-56.50	-3579.43	-40.63	-3410.65	-38.71
Benzene (C6H6)	-3301.34	-42.26	-2909.29	-36.78	-3479.66	-44.55
Benzene (C6H6)	-3169.51	-40.57	-2791.74	-35.74	-3685.62	-47.18
Benzene (C6H6)	-3169.35	-40.58	-3065.27	-39.24	-4262.68	-54.57
Benzene (C6H6)	-3301.00	-42.00	-2872.50	-36.80	-3404.00	-43.60
Benzene (C6H6)	-3304.34	-42.27	-2872.50	-36.77	-3479.71	-44.55
Benzene (C6H6)	-3982.55	-31.16	-2433.72	-38.55	-3010.85	-50.99
Hexane (C6H14)	-5835.76	-67.72	-4245.97	-49.27	-4254.50	-49.37
Toluene (C7H8)	-3771.82	-40.94	-3371.94	-36.60	-4052.76	-43.98
Toluene (C7H8)	-3947.28	-42.84	-3467.42	-37.23	-4136.52	-44.89
Toluene (C7H8)	-3769.89	-40.91	-3781.76	-41.04	-3780.53	-41.03
Toluene (C7H8)	-3769.70	-40.91	-3780.30	-41.03	-3781.60	-41.04
Heptane (C7H16)	-4501.48	-44.92	-3971.00	-39.63	-5129.70	-51.19
Octane (C8H18)	-7282.00	-63.70	-4750.00	-41.60	-5409.00	-47.00
Octane (C8H18)	-5533.30	-48.40	-4445.60	-38.90	-4366.20	-38.20
Octane (C8H18)	-7680.31	-67.25	-5951.82	-52.12	-5628.41	-49.29

Molecule	Experimental ΔHc [kJ/mol]	Experimental ΔHc [kJ/gram]	AM1 Theoretical ΔHc [kJ/mol]	AM1 Theoretical ΔHc [kJ/gram]	PM3 Theoretical ΔHc [kJ/mol]	PM3 Theoretical ΔHc [kJ/gram]
Decane (C10H22)	-9525.46	-66.94	-6883.23	-48.37	-6977.77	-49.04
Naphthalene (C10H8)	-5052.42	-39.42	-4553.69	-35.53	-5549.37	-43.30
Naphthalene (C10H8)	-5052.42	-39.42	-4553.66	-35.53	-5550.01	-43.30
"Kerosene" (C11H24)	-10447.93	-66.84	-7652.75	-48.96	-8093.57	-51.78
Kerosene (C11H24)	-7501.00	-48.00	-6034.40	-38.60	-5944.10	-38.00
Kerosene (C11H24)	-7503.00	-47.99	-6445.45	-42.22	-7652.46	-48.94
Anthracene (C14H10)	-6718.29	-37.69	-6980.77	-38.95	-6975.60	-38.92
Anthracene (C14H10)	-6935.60	-38.91	-6980.50	-39.16	-6975.30	-39.13
Phenanthrene (C14H10)	-12472.00	-69.98	-11817.21	-66.30	-13287.01	-74.55
Phenanthrene (C14H10)	-10304.61	-57.82	-7609.26	-42.69	-8093.57	-44.88
Pyrene (C16H10)	-7720.40	-38.20	-6497.70	-32.10	-6658.30	-32.90