

# CH504 - Computational Chemistry

## Lab Assignment 3

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### Question: 1

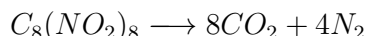
#### Aim:

To compare the thermochemical parameters such as heat of reaction using the following parameters obtained from the output file and determine the chemical energy of detonation(Q).

#### Principle:

Detonation is a process of intramolecular breakdown. It relies only on the presence of a single, suitable explosive and enough energy to simulate that breakdown. For instance, Octanitrocubane releases a great deal of energy when its highly strained carbon-carbon bonds break apart in response to a shockwave. The highly strained nature of Octa-Nitro cubane is because of small bond angles between C-C such that they have high energy density and combined with nitro groups to a strained molecule such as cubane can give compounds with enhanced high-energy density. Because high explosives do not require oxygen (or any other co-reactant), they break down much more rapidly and are much more versatile than combustible materials.

The detonation properties can be estimated based on both density and heat of formation using the following decomposition equation.



The above reaction suggests the expansion from the dense solid to gases (highly expanded due to the release of high heat of reaction) is a desirable property for a compound to be a propellant and explosive.

**Files:** CO2.log, N2.log

**Folder details:** Main Folder/ch504\_42/assignment3/q1/

#### Observation:

Compounds	E <sub>0</sub> (kcal/mol)	ZPE(kcal/mol)	H <sub>f</sub> (kcal/mol)
CO <sub>2</sub>	-117067.184	7.44529	9.68609
N <sub>2</sub>	-67,958.848	3.73488	5.809311
C <sub>8</sub> (NO <sub>2</sub> ) <sub>8</sub>	-12,07,165.179	96.6162	110.1344

## Calculations:

$$\Delta H_{298} = \Delta E_0 \Delta(ZPE) + \Delta H_T + \Delta nRT$$

$$\Delta E_0 = 8 * E_0(CO_2) + 4 * E_0(N_2) - E_0(C_8(NO_2)_8)$$

$$\Delta E_0 = 8 * (-186.5612574) + 4 * (-108.3009536) - (-1923.76921)$$

$$\Delta E_0 = -1.9246636 * 627.5 \text{ kcal/mol} = -1207.726409 \text{ kcal/mol}$$

$$\Delta ZPE = 8 * ZPE(CO_2) + 4 * ZPE(N_2) - ZPE(C_8(NO_2)_8)$$

$$\Delta ZPE = 8 * (0.011865) + 4 * (0.005952) - (0.153970)$$

$$\Delta ZPE = -0.035242 * 627.5 \text{ kcal/mol} = -22.114355 \text{ kcal/mol}$$

$$\Delta H_T = 8 * H_T(CO_2) + 4 * H_T(N_2) - H_T(C_8(NO_2)_8)$$

$$\Delta H_T = 8 * (0.015436) + 4 * (0.009257) - (0.175513)$$

$$\Delta H_T = -0.014997 * 627.5 \text{ kcal/mol} = -9.4106175 \text{ kcal/mol}$$

$$\Delta nRT = 12 * (1.9872036 * 10^{-3}) * 298 = 7.106 \text{ kcal/mol}$$

$$\Delta H_{298} = (-1207.726409) + (-22.114355) + (-9.4106175) + 7.106$$

$$\Delta H_{298} = 1232.166 \text{ kcal/mol}$$

## Relevant sections from output file:

### For Octa-Nitro cubane

```
333,-1.654822\0,3.617808,0.10536,-0.729931\0,0.515782,-3.147956,1.3816
48\0,2.491755,-2.278149,1.024788\0,1.133425,3.370293,1.083457\0,2.7577
9,1.980244,0.424311\\Version=EM64L-G09RevA.02\State=1-A\HF=-1923.76921
02\RMSD=2.708e-09\RMSF=8.507e-03\ZeroPoint=0.1539695\Thermal=0.1745692
\Dipole=0.1586015,0.5435707,0.7264094\DipoleDeriv=0.2748668,-0.0211632
,-0.0758124,-0.0282807,0.2570451,-0.0605305,-0.0281866,-0.0350536,0.05
9875,0.0622275,-0.0739434,0.0460526,-0.0946218,0.0656033,-0.0222006,0.
```

Zero-point correction=	0.153970 (Hartree/Particle)
Thermal correction to Energy=	0.174569
Thermal correction to Enthalpy=	0.175513
Thermal correction to Gibbs Free Energy=	0.104438

### For N<sub>2</sub>

Zero-point correction=	0.005952 (Hartree/Particle)
Thermal correction to Energy=	0.008313
Thermal correction to Enthalpy=	0.009257
Thermal correction to Gibbs Free Energy=	-0.012458

```
0014026123\N,0.,0.,1.0814026123\\Version=EM64L-G09RevA.02\State=1-SGG\
HF=-108.3009536\RMSD=3.398e-10\RMSF=5.838e-05\ZeroPoint=0.0059525\Ther
mal=0.008313\Dipole=0.,0.,0.\DipoleDeriv=0.,0.,0.,0.,0.,0.,0.,0.,0.,0.
,0.,0.,0.,0.,0.,0.,0.\Polar=3.9965432,0.,3.9965432,0.,0.,12.2052684
\HyperPolar=0.,0.,0.,0.,0.,0.,0.,0.,0.,0.\PG=D*H [C*(N1.N1)]\NImag=0\
-0.00004946,0.,-0.00004946,0.,0.,1.80887379,0.00004946,0.,0.,-0.000049
```

For CO<sub>2</sub>

```
Zero-point correction= 0.011865 (Hartree/Particle)
Thermal correction to Energy= 0.014492
Thermal correction to Enthalpy= 0.015436
Thermal correction to Gibbs Free Energy= -0.008824
```

```
check Guess=ICheck SCRF=Check GenChk RHF/3-21G Freq\\CO2\\0,1\C,0.,0.,
0.\0,0.,0.,1.1558716503\0,0.,0.,-1.1558716503\\Version=EM64L-G09RevA.0
2\State=1-SGG\HF=-186.5612574\RMSD=1.101e-10\RMSF=1.229e-04\ZeroPoint=
0.0118648\Thermal=0.0144921\Dipole=0.,0.,0.\DipoleDeriv=0.7647004,0.,0
.,0.,0.7647004,0.,0.,0.,2.5548942,-0.3823502,0.,0.,0.,-0.3823502,0.,0.
,0.,-1.2774471,-0.3823502,0.,0.,0.,-0.3823502,0.,0.,0.,-1.2774471\Pol
```

## Results/Conclusions:

The energy of **Detonation** comes out to be closer to **1232 kcal/mol** as per our calculations. Because of such high value of detonation energy makes Octa-Nitro cubane a suitable propellant and explosive. The results are calculated using HF/3-21G level of theory.

## Literature Comparison:

According to [this](#) paper, the value of  $\Delta H$  for the detonation reaction turn out to be -3636KJ/mol which is equal to -3636/4.184 kcal/mol = -869.02 kcal/mol which is of the same order as that of our answer.

## Extension of above concept to a new problem or situation:

Preparing such a strained molecule as Octa-Nitro cubane is highly difficult. We can extend the above concept to multiple problems of chemistry to understand the properties of organic molecules even before they are synthesized.

## Question: 2

### Aim:

To compare the Bond Dissociation Energies (BDEs) of caffeic acid and ferulic acid and determine which of them is most likely to be antioxidant

### Principle:

Caffeic acid and Ferulic acid are two phenolic compounds that exhibit antioxidant properties. The most essential structural characteristic of these two compounds, which provide effective antioxidant activity is the presence of phenolic OH groups, which enhances the ability of such molecules to quench free radicals via donating the dissociated hydrogen radical to toxic free radicals for their inactivation by neutralizing them.

Hydrogen atom Transfer (HAT) is the dominant mechanism that governs radical scavenging enthalpy (BDE). A lower BDE value signifies a higher antioxidant activity of the molecule. The BDE represents the ability of OH moiety to donate its hydrogen to a free radical by the homolytic rupture of the O-H bond represented by the following equation.

**Files:** R1lhs.log, R1rhs.log, R2lhs.log, R2rhs.log

**Folder details:** ethane Main Folder/ch504.42/assignment3/q2/

### Observation

Since we know that,

$$H_{ArO} = E(HF)_{ArO} + \text{Thermal correction to Enthalpy of ArO}$$

$$H_H = E(HF)_H + \text{Thermal correction to Enthalpy of H}$$

$$H_{ArOH} = E(HF)_{ArOH} + \text{Thermal correction to Enthalpy of ArOH}$$

**For Caffeic acid,** We have,

$$E(HF)_{ArO} = -640.7364 \text{ hartree}$$

$$E(HF)_H = -0.4961986 \text{ hartree}$$

$$E(HF)_{ArOH} = -641.293589 \text{ hartree}$$

$$\text{TCE}(\text{ArOH}) = 0.176030$$

$$\text{TCE}(\text{H}) = 0.002360$$

$$\text{TCE}(\text{ArO}) = 0.161833$$

$$BDE = H_{ArO} + H_H - H_{ArOH}$$

$$BDE = (-640.7364 + 0.161833) + (-0.4961986 + 0.002360) - (-641.293589 + 0.176030)$$

$$BDE = 0.0491534 \text{ hartree} = 0.0491534 * 627.5 = 30.843759 \text{ kcal/mol}$$

similarly **For Ferulic acid,** We have,

$$E(HF)_{ArO} = -679.5425805 \text{ hartree}$$

$$E(HF)_H = -0.4961986 \text{ hartree}$$

$$E(HF)_{ArOH} = -680.1116638 \text{ hartree}$$

$$\text{TCE}(\text{ArOH}) = 0.209736$$

TCE(H) = 0.002360  
TCE(ArO) = 0.210681

$$BDE = H_{ArO} + H_H - H_{ArOH}$$

$$BDE = (-679.5425805 + 0.210681) + (-0.4961986 + 0.002360) - (-680.1116638 + 0.209736)$$

$$BDE = 0.0761897 \text{ hartree} = 0.0761897 * 627.5 = 47.80903675 \text{ kcal/mol}$$

molecules	BDE(kcal/mol)
Caffeic acid	30.843759
Ferulic acid	47.80904

## Relevant sections from output file:

### Caffeic Acid

```
.8003165833,0.,6.1521503474\\Version=EM64L-G09RevA.02\\State=1-A'\\HF=-641.293589\\RMSD=1.908e-09\\RMSF=1.345e-05\\ZeroPoint=0.1660784\\Thermal=0.1760303\\Dipole=1.4965322,0.,2.5889897\\DipoleDeriv=0.2176946,0.,0.0905133,0.,-0.0594815,0.,0.1839462,0.,0.8789821,-0.0737702,0.,-0.0269336,0.,-0.0503604,0.,-0.0018676,0.,-0.2697516,0.0073418,0.,0.1238621,0.,-0.1954979,0.,-0.1089208,0.,0.1259066,0.9683899,0.,0.8071807,0.,0.1790109,0.,0.3911076,0.,-0.0404336,-0.0565199,0.,-0.1935784,0.,0.2138036,0.,0.
```

```
Zero-point correction= 0.166078 (Hartree/Particle)
Thermal correction to Energy= 0.176030
Thermal correction to Enthalpy= 0.176974
Thermal correction to Gibbs Free Energy= 0.128415
```

### Caffeic acid radical

```
.8614221905\\H,0.8607511439,0.,-2.3229161178\\H,2.2933851708,0.,5.182183709\\Version=EM64L-G09RevA.02\\State=2-A'\\HF=-640.7363999\\S2=1.864011\\S2-1=0.\\S2A=2.365744\\RMSD=1.684e-09\\RMSF=4.100e-05\\ZeroPoint=0.1504619\\Thermal=0.1608886\\Dipole=0.5184904,0.,1.2003323\\DipoleDeriv=-0.1345884,0.,-0.3484034,0.,-0.1294893,0.,-0.2736706,0.,-0.0312385,0.167359,0.,0.0761518,0.,0.0265986,0.,0.2368026,0.,0.2379443,-0.1133754,0.,-0.08309
```

```
Zero-point correction= 0.150462 (Hartree/Particle)
Thermal correction to Energy= 0.160889
Thermal correction to Enthalpy= 0.161833
Thermal correction to Gibbs Free Energy= 0.112745
```

### For H radical

```
\\Check Guess=TCHECK SCRF=Check GenChk UHF/3-21G Freq\\H\\0,2\\H,0.,0.,0.\\Version=EM64L-G09RevA.02\\State=2-A1G\\HF=-0.4961986\\S2=0.75\\S2-1=0.\\S2A=0.75\\RMSD=9.097e-16\\RMSF=0.000e+00\\Thermal=0.0014163\\Dipole=0.,0.,0.\\DipoleDeriv=0.,0.,0.,0.,0.,0.,0.,0.,0.\\Polar=0.,0.,0.,0.,0.,0.\\HyperPolar=0.,0.,0.,0.,0.,0.,0.,0.,0.,0.\\PG=OH [O(H1)]\\NImag=0\\0.,0.,0.,0.,0.,0.\\0.,0.,0.\\@
```

```

Zero-point correction=          0.000000 (Hartree/Particle)
Thermal correction to Energy=    0.001416
Thermal correction to Enthalpy=   0.002360
Thermal correction to Gibbs Free Energy= -0.010654

```

### Ferulic acid

```

2.093099401,0.8784433709,6.1191391471\H,2.093099401,-0.8784433709,6.11
91391471\\Version=EM64L-G09RevA.02\State=1-A'\HF=-680.1116638\RMSD=6.2
19e-10\RMSF=9.210e-05\ZeroPoint=0.1982617\Thermal=0.2097363\Dipole=0.3
665914,0.,2.860776\DipoleDeriv=0.2065334,0.,0.0527104,0.,-0.0528665,0.
,0.1425543,0.,0.9264425,-0.0423025,0.,-0.0482554,0.,-0.0516333,0.,0.05
12716,0.,-0.2806413,-0.030606,0.,0.0864277,0.,-0.2162605,0.,-0.2338223
,0.,0.0921478,1.2064893,0.,1.2482692,0.,0.2537252,0.,0.5446401,0.,0.16

```

```

Zero-point correction=          0.198262 (Hartree/Particle)
Thermal correction to Energy=    0.209736
Thermal correction to Enthalpy=   0.210681
Thermal correction to Gibbs Free Energy= 0.158919

```

### Ferulic acid radical

```

H,2.0513773246,-0.8785118526,6.1446686129\\Version=EM64L-G09RevA.02\St
ate=2-A'\HF=-679.5425805\S2=1.870129\S2-1=0.\S2A=2.384363\RMSD=1.688e-
09\RMSF=5.824e-05\ZeroPoint=0.1809584\Thermal=0.1930135\Dipole=0.84713
29,0.,1.5399746\DipoleDeriv=-0.1209756,0.,-0.3767705,0.,-0.1266808,0.,
-0.2820143,0.,-0.0560032,0.1719863,0.,0.1075993,0.,0.0237098,0.,0.2285
012,0.,0.2442565,-0.1375029,0.,-0.1478277,0.,-0.231741,0.,-0.3663005,0
.,-0.227456,0.8308835,0.,0.9725186,0.,0.2471407,0.,0.6462886,0.,0.5342

```

```

Zero-point correction=          0.150462 (Hartree/Particle)
Thermal correction to Energy=    0.160889
Thermal correction to Enthalpy=   0.161833
Thermal correction to Gibbs Free Energy= 0.112745

```

## Results/Conclusions:

Caffeic acid has smaller value of **Bond Dissociation Energy** and therefore yields more freely. Hence, we can conclude that Caffeic acid is a better anti-oxidant in comparison to Ferulic acid. One possible reason for the above observation is Caffeic radical is stabilised by H-bond while no such bonding takes place in case of Ferulic radical on radicalisation.

## Literature Comparison:

Caffeic Acid has a smaller BDE in comparison to Ferulic Acid is shown through the experiments in [this](#) which is consistent with our calculations.

## Extension of above concept to a new problem or situation:

Radicals have a very short lifetime, since they are highly reactive and unstable. They dimerize quickly and therefore, exist mostly as intermediates of a chemical reaction. However, having a knowledge of BDE of reactants tell us a lot about the mechanism of reaction and help us understand the properties of reactant. Therefore, computations such as the ones we performed here are useful for studying the reactive

properties of compounds by judging their ability to form intermediates for the reaction.