

Calculation of Activation and Reaction Energy using Gaussian

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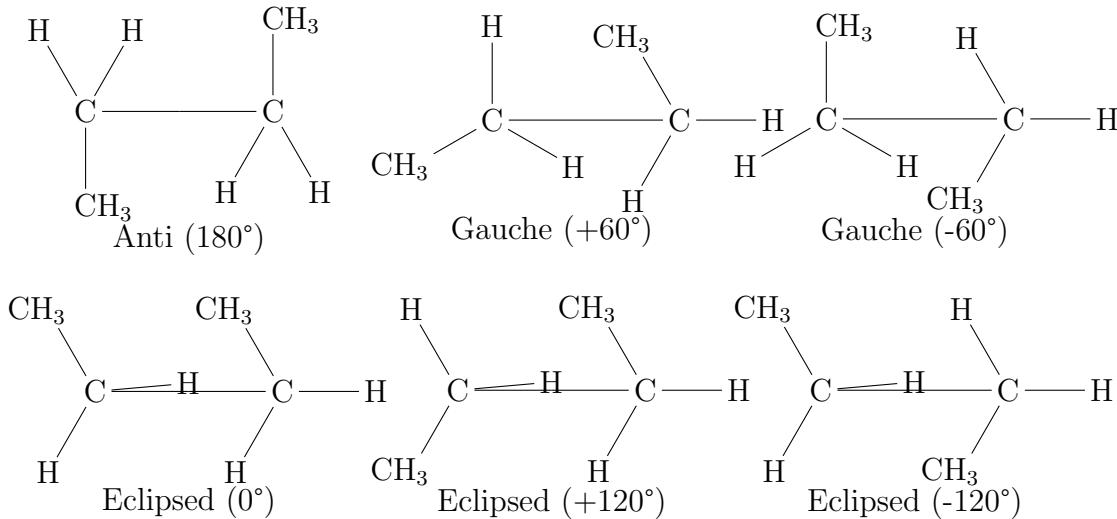
1 Conformations of n-Butane

1.1 Objective

To calculate the effect of rotation of C2-C3 bond in n-butane molecule by using the Hartree-Fock method using a computational chemistry software Gaussian.

1.2 Conformations

The six key conformations of n-butane are shown below (Newman projections):



1.3 Calculations

I used the Redundant Coordinate Editor to calculate the energy after every 10 degrees.

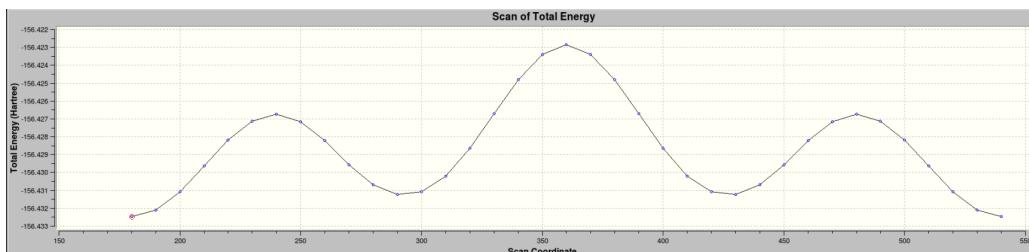


Figure 1: Graph of Degrees vs Energy

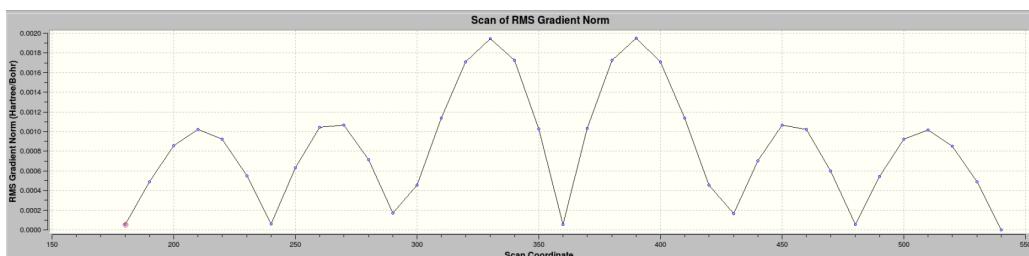


Figure 2: RMS Gradient Norm

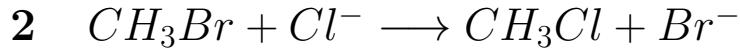
1.4 Analysis

1. It can be seen that the most stable state is the starting and the end point, i.e., when the methyl groups are at 180 degrees to each other.
2. The 2 local maxima occur at 120° and 240° when all the groups are facing each other, i.e., the non-symmetrical eclipsed state.
3. The global maximum occurs when all 4 methyl groups are in the same plane as this is the state with the most steric hindrance.

1.5 Results

File Name	nbutane.log
Calculation Type	SCAN
Method	RHF (Restricted Hartree-Fock)
Basis Set	3-21G
Charge	0
Spin	Singlet
Total Energy	$E_{\text{RHF}} = -156.43246660 \text{ a.u.}$
RMS Gradient Norm	$5.264 \times 10^{-5} \text{ a.u.}$
Imaginary Frequencies	None
Dipole Moment	0.0000 D
Point Group	C_1
CPU Time	0 d 0 h 2 min 38 s

Table 1: Gaussian output summary for conformational scan of *n*-butane.



2.1 Objective

To model the above reaction and calculate its activation and reaction energy using two different methods: HF/6-31G and B3LYP/6-31G(d,p).

2.2 Calculation of Reaction Energy

Br^-		CH_3Br	
File Name	br-	File Name	ch3br
File Type	.log	File Type	.log
Calc. Type	SP	Calc. Type	FOPT
Method	RHF	Method	RHF
Basis Set	6-31G	Basis Set	6-31G
Charge	-1	Charge	0
Spin	Singlet	Spin	Singlet
E(RHF)	-2569.81992880 a.u.	E(RHF)	-2609.35607935 a.u.
RMS Grad.	0.00000000 a.u.	RMS Grad.	0.00006262 a.u.
Imag. Freq	-	Imag. Freq	-
Dipole Moment	0.0000 Debye	Dipole Moment	2.4937 Debye
Point Group	O_h	Point Group	C_{3v}
CPU Time	2.4 s	CPU Time	6.6 s

Cl^-		CH_3Cl	
File Name	cl-	File Name	ch3cl
File Type	.log	File Type	.log
Calc. Type	SP	Calc. Type	FOPT
Method	RHF	Method	RHF
Basis Set	6-31G	Basis Set	6-31G
Charge	-1	Charge	0
Spin	Singlet	Spin	Singlet
E(RHF)	-459.52455126 a.u.	E(RHF)	-499.05657906 a.u.
RMS Grad.	0.00000000 a.u.	RMS Grad.	0.00007024 a.u.
Imag. Freq	-	Imag. Freq	-
Dipole Moment	0.0000 Debye	Dipole Moment	2.8174 Debye
Point Group	O_h	Point Group	C_{3v}
CPU Time	2.0 s	CPU Time	5.9 s

These are all the calculation summaries of the energy.
The enthalpy comes out to be: 2.587025625 kcal/mol

2.3 Calculation of Reaction Energy Method-2

CH₃Br (RB3LYP)		Br⁻ (RB3LYP)	
File Name	ch3brmethod	File Name	br-method
File Type	.log	File Type	.log
Calc. Type	FOPT	Calc. Type	SP
Method	RB3LYP	Method	RB3LYP
Basis Set	6-31G(d,p)	Basis Set	6-31G(d,p)
Charge	0	Charge	-1
Spin	Singlet	Spin	Singlet
E(RB3LYP)	-2611.62115293 a.u.	E(RB3LYP)	-2571.76135282 a.u.
RMS Grad.	0.00003969 a.u.	RMS Grad.	-
Imag. Freq	-	Imag. Freq	-
Dipole Moment	1.9383 Debye	Dipole Moment	0.0000 Debye
Point Group	<i>C_{3v}</i>	Point Group	<i>O_h</i>
CPU Time	22.3 s	CPU Time	1.7 s

Cl⁻ (RB3LYP)		CH₃Cl (RB3LYP)	
File Name	cl-method	File Name	ch3clmethod
File Type	.log	File Type	.log
Calc. Type	SP	Calc. Type	FOPT
Method	RB3LYP	Method	RB3LYP
Basis Set	6-31G(d,p)	Basis Set	6-31G(d,p)
Charge	-1	Charge	0
Spin	Singlet	Spin	Singlet
E(RB3LYP)	-460.25223339 a.u.	E(RB3LYP)	-500.11254614 a.u.
RMS Grad.	-	RMS Grad.	0.00007722 a.u.
Imag. Freq	-	Imag. Freq	-
Dipole Moment	0.0000 Debye	Dipole Moment	2.0814 Debye
Point Group	<i>O_h</i>	Point Group	<i>C_{3v}</i>
CPU Time	1.5 s	CPU Time	18.7 s

These are summaries of all the calculations.

The enthalpy comes out to be: -0.3216816 kcal/mol

2.4 Calculation Using Method-1 of Activation Energy

Transition State		Reactant	
File Name	transition	File Name	reactant
File Type	.chk	File Type	.chk
Calc. Type	FREQ	Calc. Type	FREQ
Method	RHF	Method	RHF
Basis Set	6-31G	Basis Set	6-31G
Charge	-1	Charge	-1
Spin	Singlet	Spin	Singlet
Energy	-3068.88963 a.u.	Energy	-3068.899488 a.u.
RMS Gradient	0.00002157 a.u.	RMS Gradient	0.000017 a.u.
Imag. Freq	1	Imag. Freq	-
Dipole	3.438 Debye	Dipole	11.50 Debye
Point Group	-	Point Group	-

Product	
File Name	product
File Type	.chk
Calc. Type	FREQ
Method	RHF
Basis Set	6-31G
Charge	-1
Spin	Singlet
Energy	-3068.89876836 a.u.
RMS Gradient	0.000009623 a.u.
Imag. Freq	-
Dipole	3.7771 Debye
Point Group	-

Calculation summaries

The activation energy comes out to be: 6.185869424 kcal/mol

2.5 Calculation of Activation Energy Method-2

Transition State (RB3LYP)		Reactant (RB3LYP)	
File Name	transitionmethod	File Name	reactantmethod
File Type	.chk	File Type	.chk
Calc. Type	FREQ	Calc. Type	FREQ
Method	RB3LYP	Method	RB3LYP
Basis	6-31G(d,p)	Basis	6-31G(d,p)
Charge	-1	Charge	-1
Spin	Singlet	Spin	Singlet
Energy	-3071.886109 a.u.	Energy	-3071.894191 a.u.
RMS Gradient	0.000002 a.u.	RMS Gradient	0.000004958 a.u.
Imag. Freq	1	Imag. Freq	-
Dipole	3.52 Debye	Dipole	10.6316 Debye
Point Group	-	Point Group	-

Product (RB3LYP)	
File Name	productmethod
File Type	.chk
Calc. Type	FREQ
Method	RB3LYP
Basis	6-31G(d,p)
Charge	-1
Spin	Singlet
Energy	-3071.89596667 a.u.
RMS Gradient	0.000005499 a.u.
Imag. Freq	-
Dipole	3.7791 Debye
Point Group	-

Calculation summaries

Activation energy: 5.07 kcal/mol

2.6 Comparison between Methods

2.6.1 Reference

I have taken the following as references for measurement of accuracy:

Statistical Rate Theory Calculations of the $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{ClCH}_3 + \text{Br}^-$ Rate Constant versus Temperature, Translational Energy, and H(D) Isotopic Substitution
AND

Supporting Information: The Free Energy Landscape of the SN2 Reaction $\text{CH}_3\text{Br} + \text{Cl}^- \rightarrow \text{CH}_3\text{Cl} + \text{Br}^-$ in Different Liquid Environments

2.6.2 Accuracy

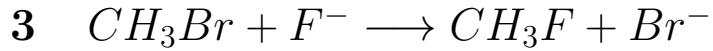
The reported values in the cited papers are as follows:

$$\Delta E = -4.7 \text{ kcal/mol}$$

$$\Delta G^\ddagger = 8.53 \text{ kcal/mol}$$

This means by our calculations:

1. HF/6-31G calculation produced 155% error in energy
2. B3LYP/6-31G(d,p) calculation produced 94% error in energy
3. HF/6-31G produced 27% error in activation energy
4. B3LYP/6-31G(d,p) has produced more accurate results overall



3.1 Reaction Energy Using HF/6-31G

CH₃F		F⁻	
File Name	ch3f	File Name	BetterF-
File Type	.log	File Type	.log
Calc. Type	SP	Calc. Type	SP
Method	RHF	Method	RHF
Basis Set	6-31G	Basis Set	6-31G
Charge	0	Charge	-1
Spin	Singlet	Spin	Singlet
E(RHF)	-138.99113857 a.u.	E(RHF)	-99.35018060 a.u.
RMS Gradient	-	RMS Gradient	-
Imag. Freq	-	Imag. Freq	-
Dipole Moment	2.3811 Debye	Dipole Moment	0.0000 Debye
Point Group	<i>C</i> _{3v}	Point Group	<i>O</i> _h
CPU Time	1.4 s	CPU Time	1.4 s

These are the summaries of the calculations.

The reaction energy comes out to be: -67.76 kcal/mol

3.2 Calculation of Activation Energy

Transition State (RHF)		Reactant (RHF)	
File Name	ch3ftransition	File Name	Freactant
File Type	.chk	File Type	.chk
Calc. Type	FREQ	Calc. Type	FREQ
Method	RHF	Method	RHF
Basis Set	6-31G	Basis Set	6-31G
Charge	-1	Charge	-1
Spin	Singlet	Spin	Singlet
Total Energy	-2708.75048167 a.u.	Total Energy	-2708.83413479 a.u.
RMS Gradient	0.00003441 a.u.	RMS Gradient	0.00002794 a.u.
Imag. Freq	1	Imag. Freq	-
Dipole Moment	9.0047 Debye	Dipole Moment	2.7542 Debye
Point Group	-	Point Group	-

Product (RHF)	
File Name	fproduct
File Type	.chk
Calc. Type	FREQ
Method	RHF
Basis Set	6-31G
Charge	-1
Spin	Singlet
Total Energy	-2708.83413490 a.u.
RMS Gradient	0.00001374 a.u.
Imag. Freq	-
Dipole Moment	2.7534 Debye
Point Group	-

These are calculation summaries.

Activation energy: **52.493 kcal/mol**

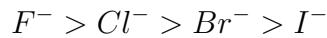
3.3 Comparison of Nucleophilicity

These are my calculation results.

3.3.1 Inference

According to our calculations, Cl^- is a better nucleophile than F^- in gaseous medium as we have obtained lower activation energy for it.

However, we know that in gaseous medium, the nucleophilic order is:



3.4 Possible Causes of Error in our Calculation

I did some research and found that these might be some probable causes for the errors:

The following factors may introduce significant quantitative errors in the computed reaction and activation energies for the gas-phase SN₂ reaction:

1. Inadequate Basis Sets for Anions

- The use of 6-31G or 6-31G(d) without diffuse “+” functions leads to poor description of the extra electron in F^- , Cl^- , and Br^- .
- This raises the energy of the anionic reactant complex and distorts the barrier height:

$$E(Y^- \cdots CH_3X) \text{ is overestimated.}$$

2. Use of the Hartree-Fock Method (RHF)

- Hartree-Fock neglects electron correlation, which is essential in describing highly charged species.
- This typically produces:

$$E_{\text{TS}}^{\text{RHF}} \text{ too low, } E_{\text{anion}}^{\text{RHF}} \text{ too high.}$$

- The resulting ΔG^\ddagger becomes artificially large.