

Determining the Effect of Substituting a Hydrogen With an Alkali Metal in the Reaction Between Ethene (C_2H_4) and Hydrobromic Acid (HBr) on the Transition State Graph using Computational Chemistry

“What is the effect of substituting a hydrogen with an alkali metal in ethene on the transition state graph of the major and minor Markovnikov reaction between ethene and hydrobromic acid using computational chemistry?”

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1. Introduction

1.1. Abstract

The reaction between ethene and hydrobromic acid is an electrophilic addition reaction leading to the formation of bromoethane. In this form, it is a relatively simple mechanism with only one outcome. However, by substituting one of the halogens in ethene with lithium, sodium or potassium, ethene becomes asymmetrical which gives rise to two isomers: the Major and Minor Markovnikov. Computational chemistry will be used to determine the transition state graphs, as vinyl sodium and vinyl potassium don't ordinarily exist. It is discovered that through the use of computational chemistry, a general pattern can be observed.

1.2. Quantum Mechanics

In the classical world, it is known exactly where something is, was and will be. The motion of classical objects is deterministic and without ambiguity given some parameters. In the world of quantum physics, particles do not behave according to these deterministic patterns. Instead, they behave with a mixture of classical and quantum properties. This wave-particle duality can be represented by a wave function, which describes the quantum state of an isolated system in terms of probabilities. The nondeterministic behaviour was largely captured by the work done by Austrian physicist Ervin Schrödinger.

To determine the behaviour of a system over time, Schrödinger proposed in his 1926 nobel-winning paper "An Undulatory Theory of the Mechanics of Atoms and Molecules",

$$H |\psi\rangle = E|\psi\rangle$$

where the Hamiltonian operator H is applied to the wave function $|\psi\rangle$ of the molecule is equal to the energy eigenvalue E of the system multiplied by the wave function (Schrödinger). Modern quantum computational chemistry attempts to find solutions for the upper-bound of the energy of a system at equilibrium, known as the ground-state energy. As

the size of the system increases and due to the complexity of electron interactions, it is known that the time taken to find a solution is an exponential relationship to the size of the system - though the true correlation is unknown - known as nondeterministic polynomial time (NP).

Since no exact solution can be found for Schrödinger's equation, it is necessary to use an approximation. The Born-Oppenheimer approximation (BO) assumes that the motion of the nuclei, in comparison with the motion of the electrons, is so small that the nuclei can be treated as a coordinate-point (Born & Oppenheimer). This allows the total energy of a system to be considered in terms of electronic and nuclear energies (Nave)

$$|\Psi\rangle_{total} = \varphi_{electronic} \varphi_{nuclear}$$

where the two systems don't interact, though the electrons do experience Coulomb potential. As the size of the system increases, BO's neglect of electron-nuclei interactions decreases the overall accuracy. For larger molecules, this becomes a problem.

1.2.1. Hartree-Fock

The Hartree-Fock (HF) ansatz assumes that a system of n fermions can be represented by n spin-orbitals by a single Slater determinant of n -by- n dimensions. For the time-independent Schrödinger's equation, HF averages the electron-electron repulsion in order to calculate the electronic energy

$$f(x_i)\chi_i = \epsilon\chi_i$$

where $f(x_i)$ is the one-electron Fock operator as represented by

$$H_{electronic} = \sum_{i=1}^n f(x_i), \quad f(x_i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^m \frac{Z_A}{r_{iA}} + v^{HF}(x_i).$$

$\frac{Z_A}{r_{iA}}$ is the coulomb attraction between the electrons and nuclei and $\frac{1}{2}\nabla_i^2$ is the combined

kinetic term for the nuclei and the electrons. v^{HF} is the potential energy from

electron-electron repulsion and asymmetry that the i -th electron experiences (Sherill). The way that x_i is changed is determined by the perturbation theory used.

1.2.2. Limitations of HF

The biggest flaw in HF is the neglect of electron correlation, which accounts for electron separability. Additionally, it determines the position of an electron solely on the position of the atom's nucleus and the average repulsion of the other electrons. As an iterable method, error increases exponentially with perturbations. However, Møller-Plesset perturbation theory (MPn) can correct some of HF's errors, decreasing the number of steps required for the ground-state energy to converge. According to Jeppe et. al. 2000, the MP series may not converge if the HF ansatz is poor (Olson & Jeppe).

1.2.3. Second Order Møller-Plesset Perturbation Theory (MP2)

As briefly mentioned, Møller-Plesset (MPn) aims to correct many of the deficiencies in HF. It does so by adding electron correlations by Rayleigh-Schrödinger perturbation theory, while using HF as an initial ansatz (Trinity College Dublin Faculty). Hence the ground-state energy of an isolated molecule is defined as

$$E_{MP2} = 2 \sum_{i,j,a,b} \frac{\langle \varphi_i \varphi_j | \hat{v} | \varphi_a \varphi_b \rangle \langle \varphi_a \varphi_b | \hat{v} | \varphi_i \varphi_j \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \sum_{i,j,a,b} \frac{\langle \varphi_i \varphi_j | \hat{v} | \varphi_a \varphi_b \rangle \langle \varphi_a \varphi_b | \hat{v} | \varphi_j \varphi_i \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

where \hat{v} is the double excited single Slater determinant, φ_i , φ_j and φ_a , φ_b are the occupied and virtual orbitals, respectively, and ϵ_i , ϵ_j , ϵ_a , ϵ_b their respective orbital energies (Møller & Plesset). Consequently, the total ground state energy is roughly defined as

$$E \simeq E_{HF} + E_{MP2}$$

for the MP2 perturbation theory. MP2 keeps computational costs low, while maintaining relatively high accuracy compared to many of its sister theories such as MP3-5 (Q-Chem Contributors). The addition of the electron correlation term causes the energy not to

converge at times, but rather, convergence can reach oscillatory, erratic or be non-existing depending on the problem (Leininger).

1.2.4. Limitations of MP2

The biggest flaw in MP2 is the limitation to unrestricted HF ansatzes. These ansatzes, in and of themselves, suffer from spin contamination arising from the spatial parts being able to differ. Mathematically, the wave function is no longer an eigenfunction of the total spin which can introduce some error (Young).

1.3. Research Question

“What is the effect of substituting a hydrogen with an alkali metal in ethene on the transition state graph of the major and minor Markovnikov reaction between ethene and hydrobromic acid using computational chemistry?”

The reaction between ethene (C_2H_4) and hydrobromic acid (HBr) lies at a complexity where the NP-hardness doesn't exceed classical computational power and contains a relatively low number of active orbitals. To answer the question “What is the effect of substituting a hydrogen with an alkali metal in ethene on the transition state graph of the major and minor Markovnikov reaction between ethene and hydrobromic acid using computational chemistry?”, a series of ground-state energy calculations, in the accurate 6-311G(d,p) basis, (Pritchard) will be performed on a locally hosted WebMO server. The 6-311G(d,p) basis set includes electron correlation terms to a high accuracy (triple-zeta quality when it comes to the simulations of valence electrons in orbitals), but it only represents hydrogen, carbon, bromide, lithium, sodium and potassium. Other basis sets which do include rubidium, caesium and francium are not as accurate. Since the increase in the size of the orbitals and number of non-valence electrons with the substitution of the alkali metals

is the largest factor contributing to shifts in the electron voltage across the orbitals, leading to changes in the ground-state energy, 6-311G(d,p) is suitable for this research.

The initial ansatz will be automatically constructed for the following reactions by the WebMO server using HF theory and perturbed using MP2.



Throughout the investigation, the reaction will occasionally be referred to as $\text{C}_2\text{H}_3\text{X} + \text{HBr}$, where X is either hydrogen, lithium, sodium or potassium.

It is expected that, as the size of the alkali metal increases, the activation energy decreases and the product energy state decreases. This is because ethene becomes more thermodynamically unstable as the C=C bond experiences greater electron-electron repulsion from the added occupied orbitals from the alkali metal. Mathematically, Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S \quad (\text{Eq. 1})$$

where ΔH is the change enthalpy, ΔS is the change in entropy, and T is the temperature in kelvin, combines the enthalpy and entropy of a system into a single value. The entropy change will be assumed to be zero. This makes the Gibbs Free Energy proportional to the change in enthalpy, which is the difference between the reactants and the products.

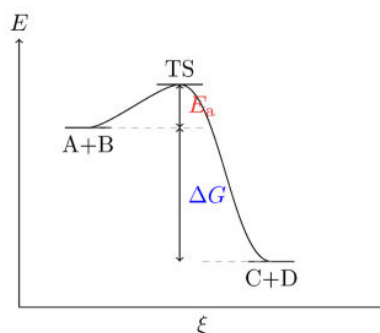


Figure 1: Irreversible Reaction. (Created by Philipp.)

By this assumption, the ground-state energy of the products should decrease as the size of the alkali metal increases, as it makes the products less stable than if it had just been with a hydrogen.

Another key feature of a transition state graph is the activation energy. The Arrhenius Equation, solved for the activation energy E_a , is

$$E_a = - \ln\left(\frac{k_1}{k_2}\right) \cdot \frac{T_2 - T_1}{T_2 T_1} \cdot R$$

where k_n is the rate constant at temperature T_n and R is the universal gas constant. The activation energy, as shown in **Figure 1**, is the energy required for a reaction to proceed (also known as the saddle point in potential energy surfaces). If the reactant becomes more unstable, then it is going to react more readily to form more stable products, releasing energy. Hence, it is expected that the activation energy will decrease as the size of the alkali metal increases.

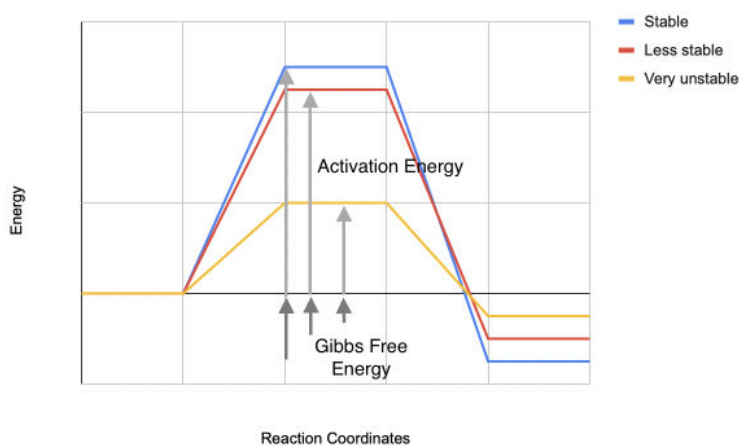


Figure 2: The expected outcome from decreasing the stability of the reactant. (Created by author.)

2. Method

2.1. Methodology

To be able to generate the transition state graphs, it is necessary to accurately represent the molecules as a wavefunction and then simulate them to find the ground-state energy for each reaction step. Then, by converting from hartrees to kcal mol⁻¹, the activation energy and enthalpy change can be calculated. The building and optimization of the molecules are done via WebMO's inbuilt software and the conversion from model to wavefunction and the running of the simulations are done with the NWChem engine.

The first step is to build the reactant state for the alkaline metal substitution and hydrobromic acid. The geometry is then optimised according to idealised mechanics. This is done in order to normalise strain energy across the reactions. Idealised mechanics are used because the ground-state energy is non-degenerate and is therefore not affected by the Jahn-Teller effect.

The second step is to build the transition state for the reactions. The ethene-like molecule C₂H₃X, where X is the alkali metal substitution (Li, Na, K), is reacted with HBr. HBr undergoes heterolytic bond fission, due to the high polarity of HBr, which causes a π bond to be broken in the C=C double bond. Since two structural isomers are possible, Markovnikov's rule applies: In the asymmetric addition of an alkene, the hydrogen will bond with the carbon with the most hydrogens already bonded.

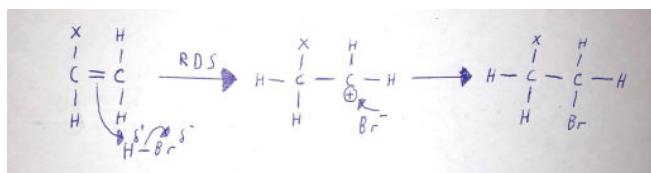


Figure 3.1: The minor Markovnikov reaction between C_2H_3X and hydrobromic acid resulting in the formation of alkyl bromide. (Created by author.)

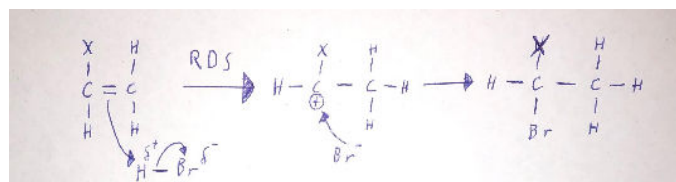


Figure 3.2: The major Markovnikov reaction between C_2H_3X and hydrobromic acid resulting in the formation of an alkyl bromide. (Created by author.)

Since, when X isn't a hydrogen, the ethene-like molecule is asymmetric, Markovnikov's rule has to be used. While both products do form, the concentration of major products, seen in **Figure 3.2**, will be much greater than the minor products, seen in **Figure 3.1**. The geometry is then optimised for both of the reactions and the strain energy normalised.

The third step is to build the product state for the minor and major Markovnikov products. For the major Markovnikov, the carbon that X is bonded to becomes positively charged. After heterolytic fission, bromide acts as a nucleophile and donates an electron to form a polar covalent bond which supposedly results in a more stable product. Oppositely for the minor Markovnikov, the bromide bonds with the carbon that X isn't bonded to.

The fourth step is to calculate the ground-state energy for each reaction step. The ansatz is constructed with HF theory and is perturbed over with MP2. This is repeated for all the substitutions, for each of the states, for both the Markovnikov. In total, 18 ground-state simulations will be run.

Ground-state energy is measured in hartrees and it is therefore necessary to convert to kcal mol^{-1} for enthalpy change and activation energy calculations (Karplus & Porter).

$$1 \text{ Hartree} = 627.503 \text{ kcal mol}^{-1}$$

To visualise the transition state, it is assumed that relative to the other states, the energy of the reactant state is zero. This allows the difference between one state to another to represent the energy change that occurs. This may be mathematically represented by

$$\Delta E_n = E_{n+1} - E_n,$$

where ΔE_n is the energy of reaction step n in hartrees. Consequently, the energy in kcal mol⁻¹ is

$$Q_n = \Delta E_n \cdot 627.503 \quad (\text{Eq. 2})$$

where Q_n is the energy of reaction step n .

By these calculations, the enthalpy change will be the product state's energy (kcal mol⁻¹). Additionally, if $Q_{\text{reactant}} > Q_{\text{product}}$, then the reaction is exothermic and the product is more stable than the reactants. Oppositely, if $Q_{\text{reactant}} < Q_{\text{product}}$, then the reaction is endothermic and the product is less stable than the reactants. It is expected that $Q_{\text{transition}}$ is always greater than Q_{reactant} . If not, then the reaction reacts spontaneously to form a stable activated complex which requires additional energy to form an unstable product.

2.1 Results

2.1.1. Major Markovnikov

The major Markovnikov reaction between C_2H_3X and HBr to form alkyl bromide, is characterised by an electrophilic attack that causes a π bond to be broken. Hydrogen acts as an electrophile due to a permanent dipole in hydrogen bromide. The hydrogen bonds with the carbon with more hydrogen substituents to form a stable carbonium ion. The bromide ion bonds with the less stable methylene-like ion to form the alkyl bromide.

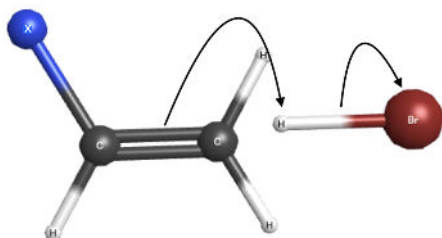


Figure 3.1. Reactant phase.
(Created by author.)

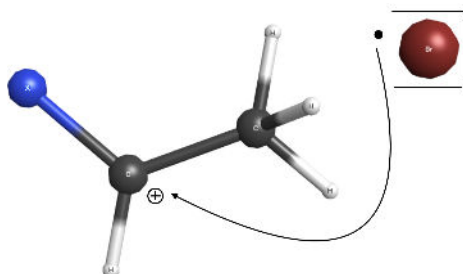


Figure 3.2. Major Markovnikov intermediate. (Created by author.)

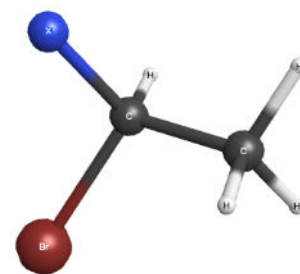


Figure 3.3. Major Markovnikov product. (Created by author.)

Reaction Step	Ground-State Energy (Hartree)			
	Hydrogen	Lithium	Sodium	Potassium
Reactant	-2650.999854	-2657.648567	-2812.223438	-3249.521488
Transition State	-2650.981109	-2657.612970	-2812.254101	-3249.561582
Product	-2651.038963	-2657.823224	-2812.260837	-3249.560929

Table 1: The major ground-state energy of hydrogen, lithium, sodium and potassium substituted for X. Note that carbon does not have a major Markovnikov reaction with hydrobromic acid.

2.1.2. Minor Markovnikov

The minor Markovnikov reaction between C_2H_3X and HBr to form alkyl bromide, is characterised by an electrophilic attack that causes a π bond to be broken. Hydrogen acts as an electrophile due to a permanent dipole in hydrogen bromide. The hydrogen bonds with the carbon with less hydrogen substituents to form a slightly more stable carbonium ion. The bromide ion bonds with the methylene ion to form the product.

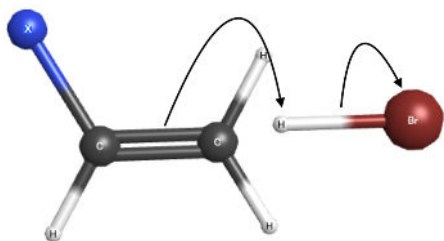


Figure 3.1. Reactant phase.

Created by author.

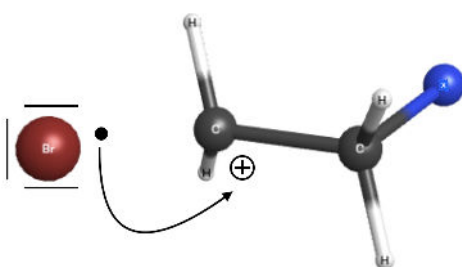


Figure 3.2. Minor Markovnikov activated complex. Created by author.

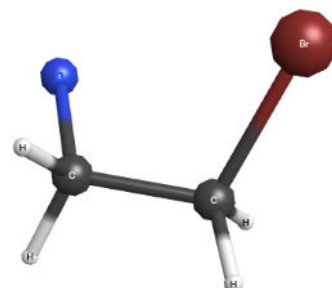


Figure 3.3. Minor Markovnikov product. Created by author.

Reaction Step	Ground-State Energy (Hartree)			
	Hydrogen	Lithium	Sodium	Potassium
Reactant	-2650.999854	-2657.648567	-2812.223438	-3249.521488
Transition State	-2650.981109	-2657.637771	-2812.247534	-3249.556336
Product	-2651.038963	-2657.628671	-2812.257246	-3249.554532

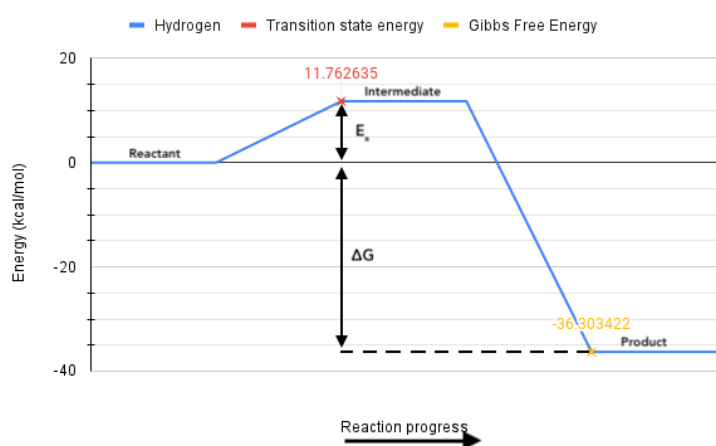
Table 2: The minor ground-state energy of hydrogen, lithium, sodium and potassium substituted for X. Note that carbon does not have a major Markovnikov reaction with hydrobromic acid.

2.2. Data processing

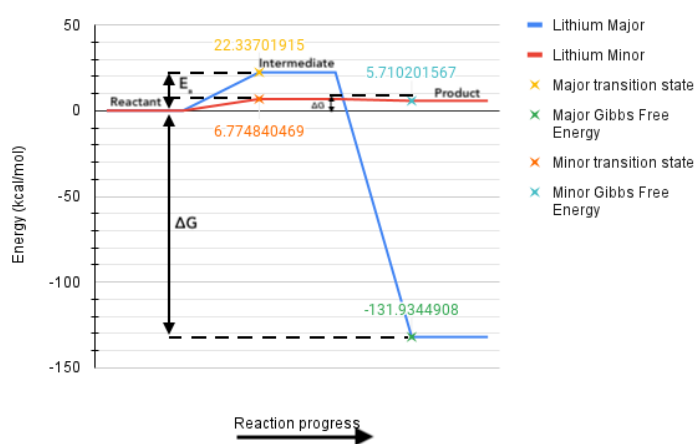
In order to construct the transition state graph, it is necessary to convert from hartrees to kcal mol⁻¹ using Eq. 2.

Reaction Step	Energy (kcal mol ⁻¹) ΔQ_n						
	Hydrogen	Lithium		Sodium		Potassium	
	H	Li Minor	Li Major	Na Minor	Na Major	K Minor	K Major
Reactant	0	0	0	0	0	0	0
Intermediate	11.762635	6.774840	22.337019	-15.12039	-19.24116	-21.86702	-25.15889
Product	-36.30342	5.710202	-131.934491	-6.094279	-4.227355	1.132272	0.409983

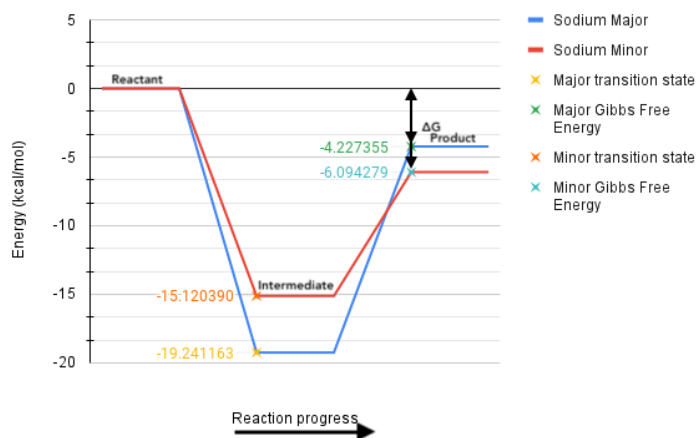
Table 3: The energy of the reactant, intermediate and product state in kcal mol⁻¹ substituted for X.



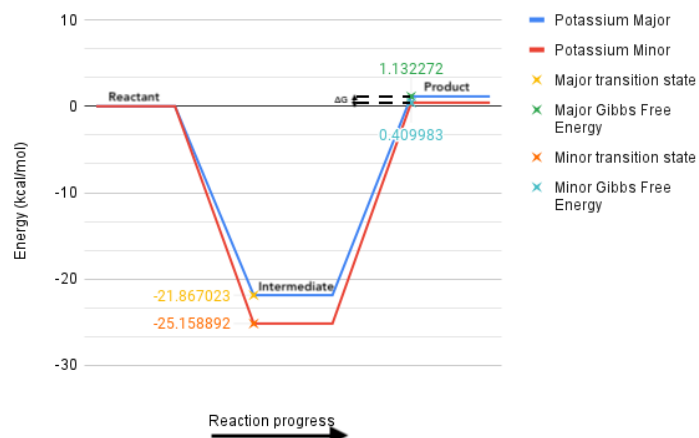
Graph 1: The transition state graph of the reaction between C₂H₄ and HBr forming bromoethane.



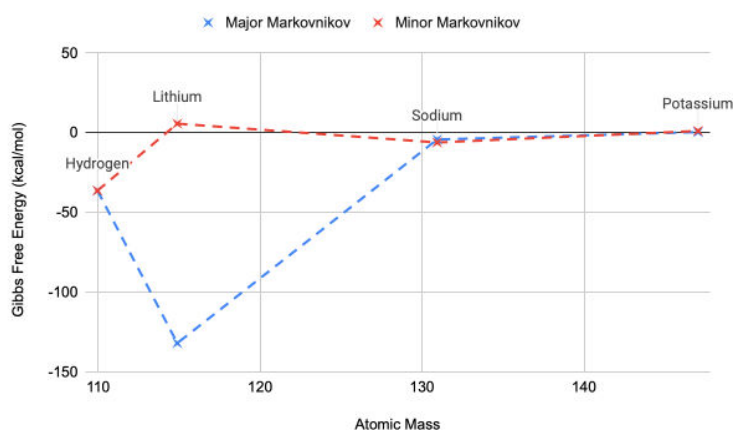
Graph 2: The transition state graph of the major and minor reaction between C₂H₃Li and HBr forming lithium;bromoethane.



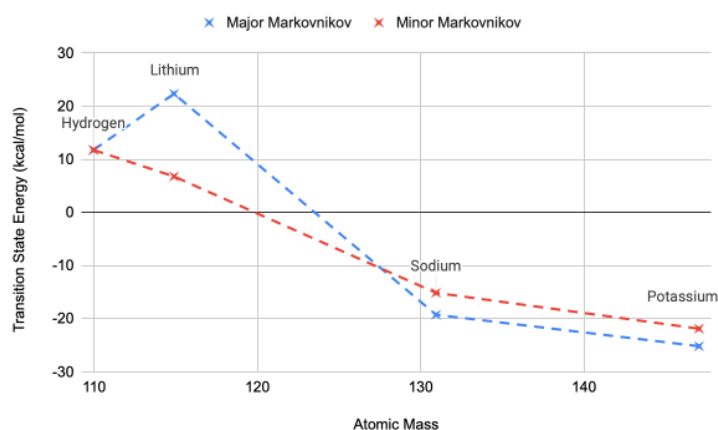
Graph 3: The transition state graph of the major and minor reaction between C_2H_3Na and HBr forming sodium;bromoethane.



Graph 4: The transition state graph of the major and minor reaction between C_2H_3K and HBr forming potassium;bromoethane.



Graph 5: The atomic mass of the product against the Gibbs Free Energy, revealing that the Gibbs Free Energy is tending towards zero. It is measured against atomic mass to ascertain a general pattern. Note that the hydrogen substitution does not have a structural isomer, but is included for comparison.



Graph 6: The atomic mass of the product against the transition state energy. It is measured against atomic mass to ascertain a general pattern. Note that the hydrogen substitution does not have a structural isomer, but is included for comparison.

3. Discussion

3.1. Patterns in the Products

When substituting a halogen in the $C_2H_3X + HBr$ reaction, it seems that the Gibbs Free Energy of both the major and the minor Markovnikov is tending towards zero (**Graph 5**). Recall that it is assumed that the Gibbs Free Energy is proportional to the enthalpy change. This suggests that, as the size of the alkali metal increases, the added orbitals from the metal are decreasing the relative difference of stability of the product to the reactants. The negative values show that the reaction is spontaneous and exothermic while the positive values show that the reaction is non-spontaneous and endothermic. The tendency towards zero could be caused by shifts in the electron density towards the metal; since the X-C bond length is greater for larger metals, the electron density shift means it is having less of an effect on the overall molecule. This could just be a case of a limited HF ansatz, which as mentioned in the introduction, only considers electrons and assumes that the nucleus is static compared to the electrons.

However, this does not explain why there is such a large difference between the major and minor Markovnikov's Gibbs Free Energy for lithium (**Graph 2**). The difference shows that the major Markovnikov product is much more stable than the minor Markovnikov, as energy is being released from the system. For the minor Markovnikov, the product may be more unstable than the reactant because of the structural geometry. By bonding to the carbon that X isn't bonded with, the differences in electronegativity values induces a dipole.

<i>Element</i>	<i>Electronegativity</i>
Carbon	2.55
Lithium	0.98
Sodium	0.93
Potassium	0.82

Table 4: Literature values for the electronegativity of carbon, lithium, sodium, and potassium.

(Values obtained from Helmensteine.)

In comparison to the major Markovnikov, the bromine amends for the difference in electronegativity by induction, where the electron density can be redistributed through sigma bonds (this effect is less effective with more sigma bonds). Since bromine and X are indirectly bonded through three sigma bonds in the minor Markovnikov, it is likely that this is why.

3.2. Patterns in the Intermediate State

In regards to the intermediate state, the general trend seems to be that as the size of the alkali metal increases, the energy of the activated complexes decreases towards a converging value (**Graph 6**). However, the hydrogen transition state is less than that lithium major. The general trend is largely explained by decreases in the highest occupied molecular orbital-lowest occupied molecular orbital (HOMO-LUMO) gap arising from the introduction of larger occupied molecular orbitals from the larger alkali metals. This causes the valence electrons, on which HOMO energy is evaluated due to the selection of active orbitals and electrons, to be further from the nucleus, causing the differences in Coulomb potential to decrease less with larger alkali metals, compared with hydrogen. LUMO energy experiences only slight decreasing changes in its energy eigenvalue due to hyperconjugation; the electrons from the sigma bond between the hydrogens and the carbon atom interact with the partially filled p-orbital in the carbonium ion which stabilises the activated complex.

A higher HOMO energy means a compound is more electron deficient and a lower LUMO energy means a compound is more electrophilic. A positive HOMO-LUMO gap indicates HOMO energy is greater than LUMO energy which means that a compound is more stable. On the other hand, a negative HOMO-LUMO gap indicates that LUMO energy is greater than HOMO energy which means that the compound is not stable. The gap ranges from ≈ 22 to ≈ -22 for the major Markovnikov and ≈ 6 to ≈ -25 , as seen in **Graph 2, 3, and 4**. From this, it can be concluded that the sodium and potassium substitutions are not stable, whereas the lithium substitution is.

In regards to the intermediate state energy of ethene being less than the major lithium-substituted ethene, steric hindrance may be the reason. The lithium is much larger than the hydrogens and will push the other hydrogens towards the carbonium ion due to steric bulk. This makes the energy state of the activated complex higher for the major lithium-substitution than for ethene, as seen in **Graph 6**. The same thing could be said for the minor lithium substitution where the distance between the lithium and the positive ion reduces the effect of steric hindrance. Overall, a higher positive value for the intermediate state energy suggests a slower reaction that requires more energy than intermediate states of lower energy.

Furthermore, **Graphs 3 and 4** both have negative transition state energy. This suggests that the reaction would not ordinarily reach the product state as the transition state is more stable. By substituting sodium and potassium, it is likely that it changed the reaction mechanism and that this has caused other products like sodium and potassium bromide salts to be more likely to form. Sodium and potassium both have less effective nuclear charges than lithium. This may contribute to decreased oxidising power in the carbonium ion, as a dipole is created between the sodium/potassium and the carbonium ion that is greater than the dipole created between the lithium and the carbonium ion (see **Table 4** for reference). The bromide ion will then have a hard time to bond with the carbon as the dipole reduces the carbon's ability to accept an electron.

3.4. Reaction Mechanism

In regards to the reaction mechanism, changes in the general shape of the transition state profile as discussed in sections 3.2 and 3.3 and highlighted in **Graph 1, 2, 3, and 4** suggests that the reaction did not proceed as expected. This is caused by the orbital from which substitution polarises to; lithium and hydrogen lose electrons from their $2s^1$ and $1s^1$ orbitals and is left with a $1s^2$ and $1s^0$ where as sodium and potassium lose electrons from their $3s^1$ and $4s^1$ orbitals and are left with $[\text{He}]2s^22p^6$ and $[\text{Ne}]3s^23p^6$. This may be what changes the nature of the bond from covalent to ionic as the molecular orbitals are split such that they are more distributed over the carbon. Consequently, it is more likely that a bromide salt since they are heteronuclear diatomics.

3.5. Extension

It is plausible that similar patterns could be found if the simulations were extended to rubidium, caesium and francium, as they contain more orbitals of greater size. However, current basis sets are poor in representing these large molecules and the computational cost would be very high.

The experiments could also be done with Couple Cluster Single and Double Theory (CCSDT), which is considered the golden standard of computational chemistry. It considers the single and double excitation and can more accurately represent electron correlation terms.

Lastly, physical experiments could be done to try and verify the results. Though the sodium and potassium substitutions are exotic, ethene, vinyl lithium and hydrobromic acid are readily available from a number of manufacturers. It is difficult to ascertain exactly which pathway a chemical reaction will take place, so it would not only be useful to verify the research but also as an extension into why it prefers some reactions over others.

4. Conclusion

To answer the question, “What is the effect of substituting a hydrogen in ethene with an alkali metal on the transition state graph of the major and minor Markovnikov reaction between ethene and hydrobromic acid using computational chemistry?”, the activated complex’s energy, generally, becomes more negative with each substitution appearing to converge at some unknown value. This pattern does not hold true for the comparison between the hydrogen and major lithium substitution, where the introduction of additional electrons improves the stability of the reactant and requires more energy to overcome the energy barrier. In regards to the products, substituting alkali metals of larger size causes the ground-state energy to converge towards the ground-state energy of the reactant. For hydrogen, lithium major and sodium substituted for X, the reaction is exothermic. The reaction is endothermic for lithium minor and potassium.

Though there are no literature values to compare the validity of the experiment to, the basis set, ansatz theory and perturbation theory are commonly used in computational chemistry. The 6-311G(d,p) basis set is of triple-zeta quality when it comes to the simulation of valence electrons in orbitals. MP2 is common practice in simulating quantum dynamics and is a reliable optimization technique which accounts for some of the deficiencies of HF.

However, HF theory may not have been the best ansatz theory to use for this investigation. Since HF (without MP2) considers electron energy largely independent of other electrons, the added energy from additional orbitals - which was a large source of the pattern - is omitted. It is seen in this investigation, however, that it did have an effect which can be attributed to MP2. A more appropriate ansatz theory could’ve been Density Functional Theory which calculates the ground-state energy based off of the electron density. This is more accurate as orbitals are largely just centres of electron density.

Another source of limitations comes from the use of WebMO. As it is free-to-use, it may only satisfy introductory-level accuracy and it may be necessary to perform the same

optimizations on more professional, paid software as it will have the funding to implement state-of-the-art geometry optimization techniques, in order to receive more accurate results.

There is also the problem of stochasticity in solving Schrodinger's equation. Heisenberg's uncertainty principle states that the more information one collects about the position of the electron, the less certain you can be of its future position. This causes early approximations within HF and MP2 that can exponentiate errors and decrease confidence in the final result.

Much is still not understood about the field of quantum mechanics. As the founder of quantum computing and nobel prize winner Richard Feynman once said, "If you think you understand quantum mechanics, you don't understand quantum mechanics" (Feynman). With still much unknown about the field, it is plausible that the explanations given for the patterns may only be part of a greater explanation. To expand upon the investigation, one could look to see if the pattern held true for similar reactions such as the electrophilic aromatic substitution of benzene. Furthermore, would the pattern stand if expanded to rubidium, caesium and francium as well?

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