Energy Profile and Temperature Dependence of Product Yields for Electrophilic Addition in Linear Conjugated Systems

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Abstract

This work involves the reaction mechanism and energetics of isomeric product formation in electrophilic addition reactions of linear conjugated systems. The specific reaction reported in this paper involves the addition of HBr to 1,3-butadiene to form two isomeric products, 3-bromo-1-butene and (E+Z)-1-bromo-2-butene. Gaussian computational methods were used to determine the energy profile for each reaction pathway leading to a single isomer and their corresponding activation energies. A qualitative analysis of the computationally predicted kinetics and thermodynamics of the reaction pathways shows a consistent positive trend between the computational prediction and the experimental product yields.

Introduction

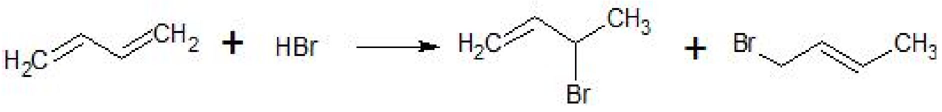
Earlier studies have shown that molecular geometry is affected by ionization. Both bond lengths and bond angles seem to be drastically affected by ionization, or electron removal. The removal of an electron in unsaturated systems such as trifluoromethylperoxynitrate (CF_3OONO_2) showed both ionization effects upon bond lengths and bond angles (Yao *et al.*, 2007). Likewise, significant changes in molecular geometry from the ionization of both $FC(O)SSCH_3$ and FC(O)SSSC(O)F were observed. The $FC(O)SSCH_3$ molecule transforms into a heavy atom planar structure after ionization, whereas FC(O)SSSC(O)F shows different behavior. The FC(O)SSS part becomes planar while the C(O)F part remains in its original geometry (Erben and Della Védova, 2002). Also, the removal of an electron has shown effects on electron density. Melin has studied this and has determined that there is an increase in electron density in specific regions due to ionization. He also found that there were cumulative effects from multi-electron removal using ab initio and density-functional theory (DFT) calculations (Melin *et al.,* 2007). Previous studies have shown how electron removal can affect a molecule, but one might wonder how ionization would affect a linear conjugated system. Losing an electron may not be expected to have significant effect on the electron density distribution of the molecule, but it could affect the stability, perhaps. Linear conjugated systems can be studied specifically to see if the stability of the system breaks down from ionization, since any change in geometry would be noticed more easily with linear structures. It was noted that the precise changes in molecular geometry and alteration of bond length by ionization were unknown in conjugated systems (Kunii and Kuroda, 1968). Although this information was stated in 1968, no updated information has been found regarding the geometry and change in bond length from ionization. The first goal of this project is to calculate the changes in the properties of conjugated systems by the process of ionization using established computational methods.

Computational approaches are used to determine the electron densities and other structural affects for various compounds. The Gaussian approach uses both ab initio and semi-empirical methods to approximate the calculations. Ab initio methods are based upon quantum mechanical principles. However, the calculations are not exact and contain a small margin of error. Ab initio methods are more accurate than the semi-empirical methods which include further approximations leading to higher error (Kruse, 2010). Both DFT and Hartree-Fock Theory (HF) are ab initio methods. DFT has been known to give better results for electron densities, bond lengths, and vibrational frequencies in comparison to HF, according to Wang *et al*. The comparison of various methods to the DFT theory shows that the DFT electron densities are very similar to the high level ab initio results at distances farther away from the nuclei (Wang *et al.*, 1996).

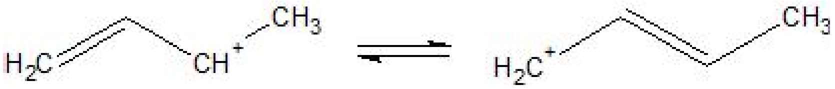
However, results vary from molecule to molecule. Some semi-empirical methods are more accurate for conjugated systems. Semi-empirical methods are much quicker than ab initio methods because of approximations of some empirical parameters. Because of these approximations, calculations for large molecules such as proteins are possible within a much shorter time frame. The Parameterization Model 3 (PM3) is a type of semi-empirical method that was derived from other semi-empirical methods such as the Modified Neglect of Differential Overlap (MNDO) and the Austin Model 1 (AM1). MNDO approximates 2-electron integrals and 1-electron terms. The extended Hückel approach is used in some of the approximations and AM1 was introduced to adjust some nuclear repulsion energy parameters. Further adjustment of this approach, gave rise to PM3 (Jensen, 2010). Potentially, PM3 could give better results than DFT.

Hückel orbital energies have been proven useful for unsaturated hydrocarbons (Brogli and Heilbronner, 1972). These predictions are only applicable to the π orbitals of conjugated systems. Since Hückel theory is known to be accurate for determining π orbital energies in conjugated systems, in this study it is used to determine the effect of ionization on the π orbital energy while DFT/B3LYP and PM3 methods are used to determine the same effect on the overall molecular energy of the conjugated system. Based on the comparison of the changes in π energy and the molecular energy upon ionization, further insight into the effects of ionization are gained.

For purpose of comparison, one might investigate what stability effects would occur if a conjugated system was ionized through a reaction. The electrophilic addition of hydrogen bromide to 1,3-butadiene is an example of this.



It is proposed that 1,3-butadiene is “ionized” by the addition of a proton in the formation of the reaction intermediate (Carey and Giuliano, 2014). The carbocation intermediate formed from the addition of a proton is related to the ionized structure formed from the removal of an electron, because in both cases, the conjugation in the system is disrupted leading to alternate distributions of π electrons. The proposed reaction mechanism occurs in two steps: first by the addition of H^+ followed by the addition of Br^-. The intermediate created is a carbocation that has two resonance forms:



These resonance forms give two different products upon addition of bromide. One product is formed by 1,2 addition and the other is formed by 1,4 addition. The 1,2 addition product, or 3-bromo-1-butene, is known to be the kinetically controlled product, and the 1,4 addition product, (E+Z)-1-bromo-2-butene, is known to be the thermodynamically controlled product (Carey and Giuliano, 2014). The intermediate step in this reaction also follows Markovnikov’s rule, “[W]hen an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogens, and the halogen adds to the carbon that has fewer hydrogens” (Carey and Giuliano, 2014). Therefore, the 1,2 addition product formed is the kinetic product due to the greater stability of the carbocation intermediate. The secondary carbocation is formed quicker than the primary carbocation.

There have been some previous experimental studies to verify Markovnikov’s rule. At -80°C, the percent yield of the two products were found to be 81% 3-bromo-1-butene and 19% (E+Z)-1-bromo-2-butene. And at 45°C, the percent yield of the two products was 15% and 85%, respectively. The transition of the predominant product changes around room temperature (Carey and Giuliano, 2014). These results agree with kinetic and thermodynamic control. At lower temperatures, the kinetic product is more predominant whereas at higher, the thermodynamic product is the predominant species. One would expect that the equilibrium between the two products would be established over time and the thermodynamic product would eventually become the major product due to its higher stability.

No published computational results for electrophilic reactions were found that gave values of activation energy and reaction energy profile plots that are consistent with the experimental product yields for kinetically and thermodynamically controlled mechanisms. Therefore, in this study energy calculations for electrophilic addition reactions have been extended beyond the formation of carbocation intermediate to give a complete reaction energy profile in agreement with Markovnikov’s rule and the experimental results.

Methods

The software used for the purpose of this study was Spartan Student Edition Version 6. Computational methods available with this software include MMFF94, PM3, HF, DFT (B3LYP & EDF2), and MP2. Ionization calculations were performed using DFT (B3LYP/6-31G*), HF (6-311+G**), and PM3. The molecules were calculated using the geometry optimization function that lasted between 1 and 33 minutes per molecule. Hückel Theory calculations determined the π energies of the molecules in less than 1 minute per molecule.

Studying the electrophilic addition reaction involved the same three methods that were used for ionizations. Calculations were performed by constraining bond distances and bond angles from the reactant to product and vice versa. Each step of the reaction mechanism included at least 11 consecutive computations. Computations took under 15 minutes for each step.

Ionization Data for Comparison of Computational Methods

The molecules studied include 1,3-butadiene, 1,3-pentadiene, 1,3,5-hexatriene, 1,3,5-heptatriene, 1,3,6-heptatriene, and 1,3,5,7-octatetraene. These molecules were studied in both *cis* and *trans* forms as well as with a methyl substituent attached to the 2-carbon of the *trans* form. The ionization energies were calculated using DFT, PM3, HF, and Hückel Theory. The Hückel ionization energies were plotted against the HOMO energy coefficient from Hückel Theory.

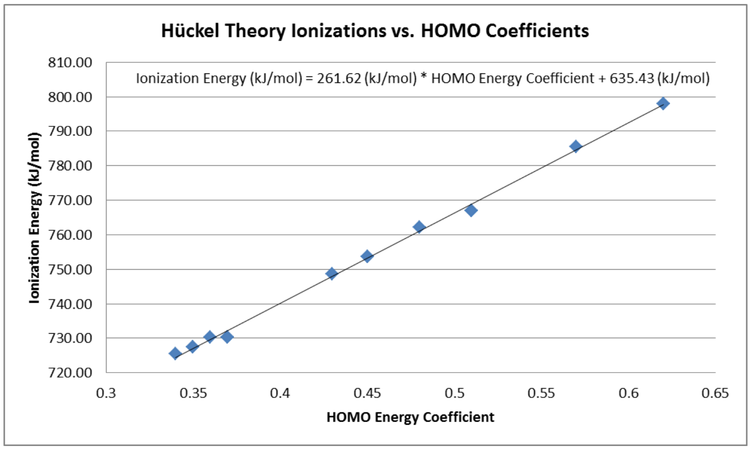


Figure 1: Linear trend between the ionization energy and the HOMO energy coefficient.

Assuming that the Hückel theory is accurate for determining π orbital energies in conjugated systems, the three methods were all compared to Hückel Theory.

Table 1: The differences in quantum mechanical molecular energies with ionization are compared to the differences in Hückel Theory's π energy. DFT showed the lowest difference in ionization energy in comparison to Hückel Theory, followed by PM3 and HF.

Ionization Energy Comparison to Hückel Theory

Compound	DFT Difference (DFT-Hückel) (kJ/mol)	PM3 Difference (PM3-Hückel) (kJ/mol)	HF Difference (HF-Hückel) (kJ/mol)
trans-1,3-butadiene	-19.07	-61.99	84.75
(3E)-1,3-pentadiene	-2.94	-58.92	91.05
(3E)-1,3,5-hexatriene	24.55	-38.46	120.07
(3E,5E)-1,3,5-heptatriene	33.39	-39.33	122.43
(3E,5E)-1,3,5,7-octatetraene	54.50	-21.20	148.71
cis-1,3-butadiene	-20.07	-68.93	80.73
(3Z)-1,3-pentadiene	-4.94	-60.43	88.48
(3Z)-1,3,5-hexatriene	20.55	-47.64	114.77
(3Z,5Z)-1,3,5-heptatriene	27.39	-41.95	113.55
(3Z,5Z)-1,3,5,7-octatetraene	46.50	-31.08	141.03
trans-2-methyl-1,3-butadiene	-12.61	-58.66	90.15
(3E)-2-methyl-1,3-pentadiene	6.23	-51.94	99.44
(3E)-2-methyl-1,3,5-hexatriene	28.73	-36.28	123.50
(3E,5E)-2-methyl-1,3,5-heptatriene	42.39	-33.84	128.01
(3E,5E)-2-methyl-1,3,5,7-octatetraene	58.57	-19.10	150.86
Average	18.88	-44.65	113.17

Reaction Energy Data for Comparison of Computational Methods

The 1,2-intermediate, 1,4-intermediate, and the resonance structure of the electrophilic addition reaction all underwent an energy calculation. Using every method available on Spartan Student Edition Version 6, their energies were calculated.

Table 2: Only three of the twelve available methods agreed with both Markovnikov’s rule and resonance theory. These were PM3, HF/6-31G*, and HF/6-311+G**. PM3 showed the most accurate results and was used for the remaining computations.

Energy of Reaction Intermediates			
Method	1,2-Intermediate Energy (kJ/mol)	Resonance Structure Energy (kJ/mol)	1,4-Intermediate Energy (kJ/mol)
MMFF	-280.28	-274.01	-301.43
PM3	341.11	276.37	346.86
HF/STO-3G	-7083888.63	-7083992.52	-7083910.40
HF/3-21G	-7127740.89	-7127823.36	-7127746.60
HF/6-31G*	-7161158.02	-7161224.69	-7161152.68
HF/6-311+G**	-7161971.58	-7162032.52	-7161963.04
B3LYP/6-31G*	-7168733.34	-7168799.91	-7168743.06
B3LYP/6-311+G**	-7169549.24	-7169613.08	-7169556.99
EDF2/6-31G*	-7169684.98	-7169751.33	-7169693.72
EDF2/6-311+G**	-7170503.41	-7170567.12	-7170510.16
MP2/6-31G*	-7162762.89	-7162843.75	-7162775.18
MP2/6-311+G**	-7163774.92	-7163850.47	-7163783.75

Using PM3, the overall reaction energy profile was computed stepwise first from 1,3-butadiene to the resonance structure of the reaction intermediates and then to the two products.

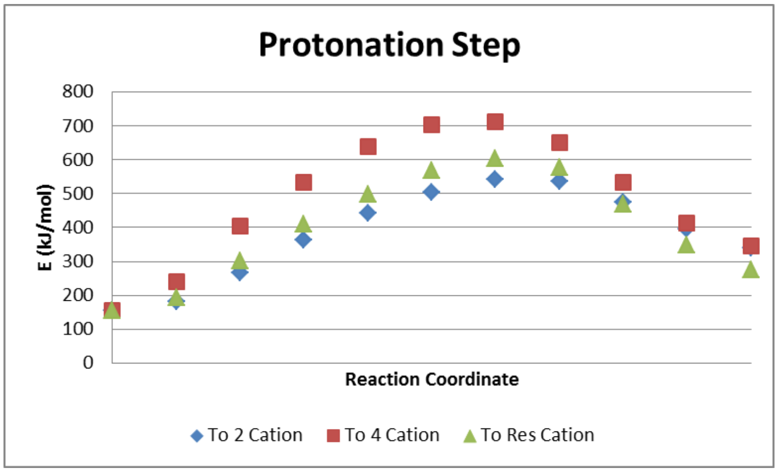


Figure 2: The first step of the reaction was calculated from 1,3-butadiene to the 1,4-intermediate, 1,2-intermediate, and resonance structure of the two intermediates. The lowest energy value per step was used for the overall plot; therefore, the path of reaction is from 1,3-butadiene to the resonance structure.

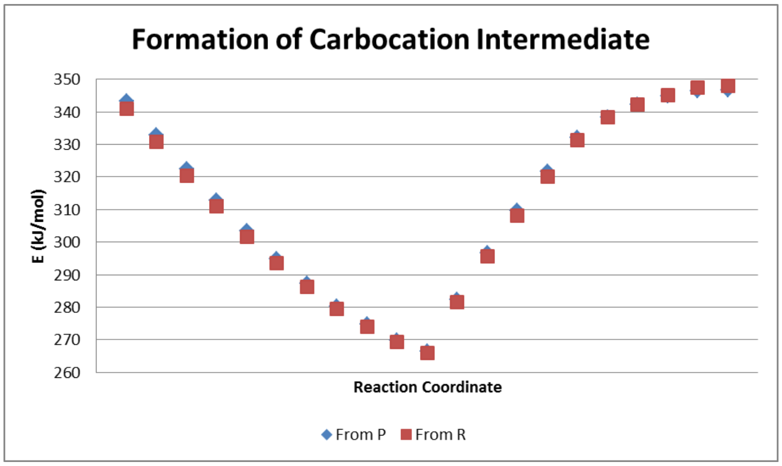


Figure 3: The step of the reaction that converts intermediates is displayed. The lowest part of the plot represents the resonance structure of the two intermediates. This step of the reaction was calculated from 1,2-intermediate to 1,4-intermediate and vice versa. The lowest energy value per step was used for the overall plot.

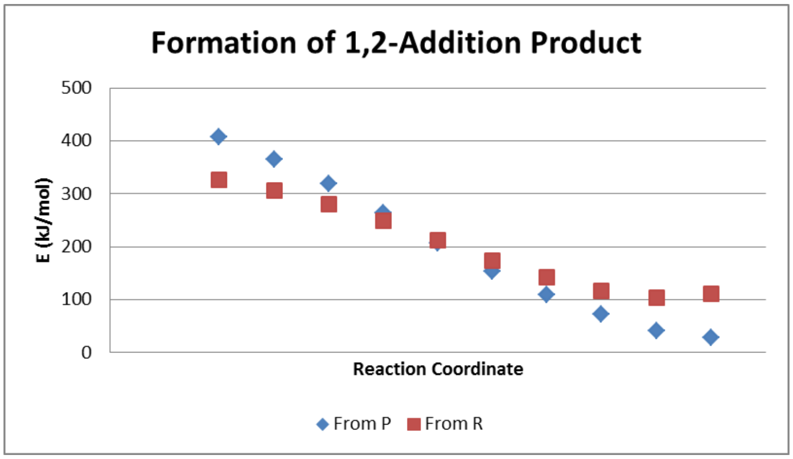


Figure 4: This step involves the reaction path from the 1,2-intermediate to the 1,2-product. This plot was calculated using the same method as figure 3.

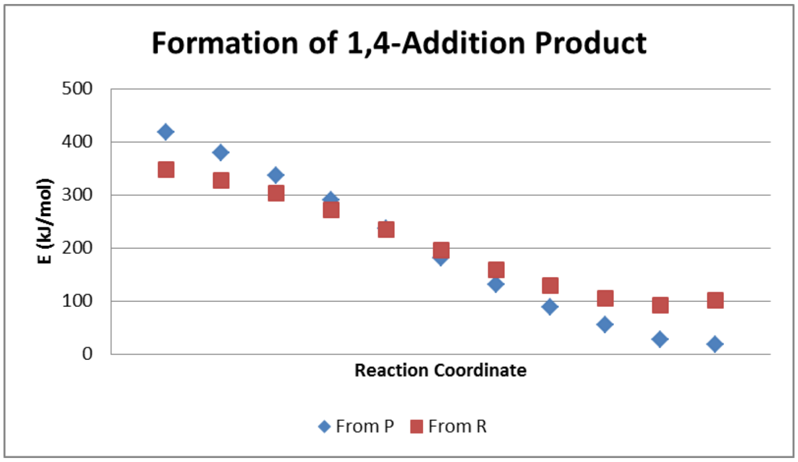


Figure 5: The This step involves the reaction path from the 1,4-intermediate to the 1,4-product. This plot was calculated using the same method as figure 3.

Putting together figures 2 through 5, the overall reaction mechanism was modeled.

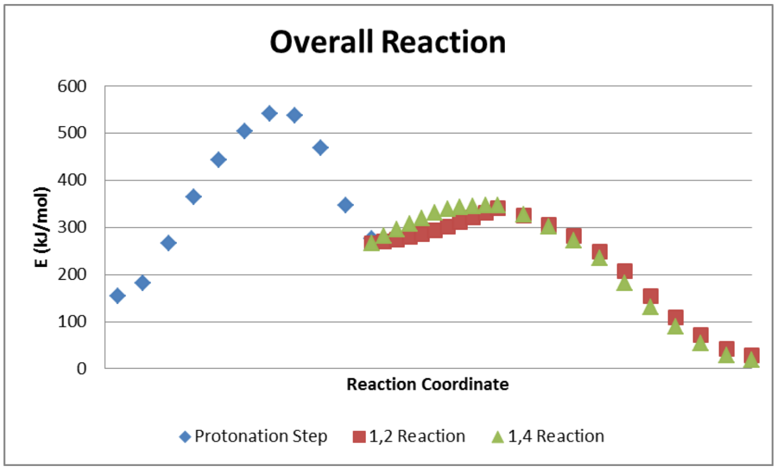


Figure 6: After the resonance structure of the intermediates is formed, the path of reaction can go in two separate ways. The peak of this second step represents the activation energy for the formation of carbocation structure. Comparison of the molecular energies of the two products shows that the 1,4-addition reaction product has greater stability.

Table 3: The calculated activation energies of the overall reaction. The first step of the reaction showed much higher activation energy relative to the second step's activation energy. Comparison of the second step activation energies for the two products shows that the 1,2-addition reaction has a lower activation energy.

Activation Energies		
Pronation Step	1,2-Product Formation	1,4-Product Formation
387.64 kJ/mol	64.89 kJ/mol	70.55 kJ/mol

After the initial reaction takes place, an equilibrium is established between the two products. The equilibrium reaction energy profile was calculated similarly to the overall reaction plot.

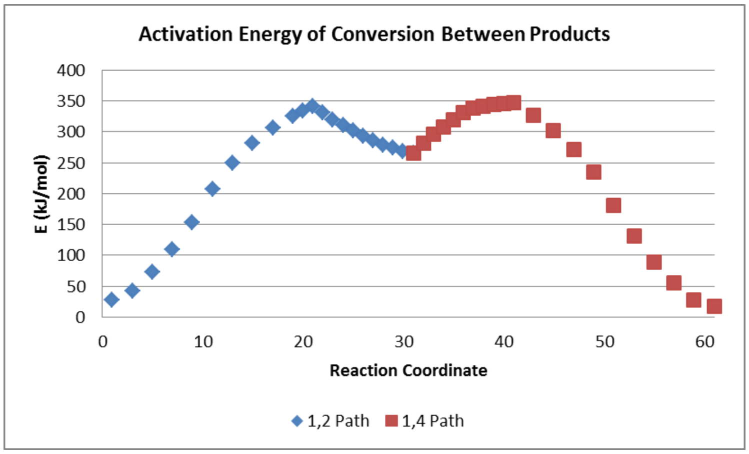


Figure 7: The equilibrium plot is displayed showing the conversion between the two products. One product proceeds to the resonance structure before fully converting to the other product.

Table 4: Comparison of the two activation energies for the conversion between products. The conversion from 1,2-product to 1,4-product requires less activation energy than the reverse process.

Equilibrium Activation Energy	
From 1,2-Product	From 1,4-Product
313.07 kJ/mol	328.79 kJ/mol

Combining both kinetic and thermodynamic properties, relative product yields can be predicted. The relative yields have a temperature dependence and has to be calculated at each temperature.

Table 5: Kinetic and thermodynamic properties of the electrophilic addition reaction. Comparing these properties results in the prediction of relative product yields.

Relative Product Yields and Temperature Dependence			
Temperature (K)	Thermodynamic Ratios ($K_{1,4}/K_{1,2}$)	Kinetic Ratios ($k_{1,2}/k_{1,4}$)	Percent Relative Yield of 1,4-Product (%)
190	58.63	35.98	61.97
193	58.67	34.03	63.29
200	58.74	30.08	66.14
210	58.80	25.58	69.69
220	58.81	22.07	72.71
225	58.81	20.60	74.05
230	58.79	19.29	75.29
240	58.73	17.05	77.49
250	58.63	15.23	79.39
260	58.52	13.71	81.02
270	58.37	12.44	82.43
280	58.21	11.37	83.66
290	58.03	10.46	84.73
298.15	57.87	9.81	85.51
300	57.83	9.67	85.67
310	57.62	8.99	86.50
318	57.44	8.51	87.10
320	57.39	8.39	87.24
325	57.27	8.12	87.58
330	57.15	7.87	87.90

Discussion

The effects of ionization in conjugated molecules have revealed several trends. The major effect is that molecular stability decreases with ionization. This effect has already been established by other earlier studies (Kunii and Kuroda, 1968) and was verified through this computation showing an increase in overall energy by the removal of an electron. Also, as the conjugated system's length increased, ionization energy decreased (i.e. molecular energy increased). *Cis* and *trans* forms of these systems had no effect on the ionization energy, and adding a methyl substituent decreased the ionization energy. Changes in the ionization energy can be explained with the β parameter coefficient of HOMO energy level which can be calculated from the Hamiltonian matrices in Hückel Theory. . The β parameter describes the resonance or bond integrals and is an approximate value for π bonds formed from overlap of two C2p atomic orbitals (about −2.4 eV or −230 kJ/mol). As the coefficient of β for the HOMO energy level decreases, overall molecular energy increases and the ionization energy decreases. The decrease in this coefficient brings the energy level closer to the antibonding energy level, requiring less energy to remove an electron from the HOMO. Increasing the conjugated system length decreases its stability, because the system becomes longer and less compact, increasing its overall energy. Adding a methyl substituent has a similar effect on a conjugated molecule. The addition of a substituent increases the length and size of the molecule and removes the structural equality between the carbon atoms. *Cis* and *trans* forms of these systems had no effect on the ionization energy because each form has very similar overall energy. According to Hückel Theory, their π energies are equal to each other. Hence, removing a π electron from either form would be the same.

The overall molecular energy increase with ionization was calculated using different levels of theory and was found to be comparable to the π energy increase with Hückel Theory that is observed with the removal of an electron from a π orbital. Density functional theory (DFT/B3LYP 6-31G*) compared the best to Hückel Theory averaging only 18.88 kJ/mol below Hückel's predictions. Parameterized Model 3 (PM3) averaged 44.65 kJ/mol over, and Hartree-Fock (HF 6-311+G**) averaged 113.17 kJ/mol under Hückel's predictions. DFT had been known to give accurate results for ionization in other studies, and these results verified that the same applies for the ionization of linear conjugated systems.

Based on the good DFT results of ionization by electron removal from conjugated systems, it was expected that DFT would also give good results for a reaction that proceeds through an *ionized intermediate* in conjugated systems. Electrophilic addition of 1,3-butadiene and hydrogen bromide goes through an ionized state by a protonation process instead of an electron removal. Using the three methods mentioned above, the reaction mechanism was predicted to go through a protonation and bromination steps. The reaction progress was simulated by constraining bond lengths and adjusting bond angles from reactant to product. In the protonation step, the reaction proceeds from 1,3-butadiene to the resonance structure of the two carbocation intermediates. This step has a large activation energy. In the second bromination step, the reaction path goes through either C-2 carbocation or C-4 carbocation with different activation energies. Once bromination of the carbocation begins, the overall energy of the molecule decreases toward the product.

Markovnikov's rule indicates that when comparing the two paths in this reaction, the 1,2-intermediate should have lower activation energy. Every method available in Spartan Student Edition Version 6 was used to determine which of these methods agreed with the results predicted by Markovnikov's rule. As it turned out, DFT did not produce the results expected. Instead, PM3 and HF (6-31G* and 6-311+G**) were the only methods that agreed with the Markovnikov's rule. Therefore, it was established that DFT is an accurate method for the ionization by electron removal but not for the protonation of a molecule.

Based on the overall reaction plot computed with PM3, the activation energy of the protonation step is 387.64 kJ/mol. For the 1,4-reaction path, the activation energy is 70.55 kJ/mol while the 1,2-reaction path has an activation energy of 64.89 kJ/mol. It is also noticeable that the reaction is exergonic irrespective of the kind of product formed. During the second step of 1,2-addition or 1,4 addition of bromide, various factors such as temperature can affect the path of reaction. The two products have slightly different molecular energies from each other. The 1,4-product has lower molecular energy than the 1,2 product. Because the only difference in the reaction is in the second step when the reaction can go in either of two paths, the activation barrier in the second step will determine the kinetically controlled relative yields of the two products. If the kinetic energy of the reactants is low, the reaction path will go in the direction of lower activation energy. This would favor the 1,2-addition product. However, thermodynamically, the more stable product will have the higher yield if there is enough energy to overcome the activation barrier. This prediction has been proved to be the case experimentally since the kinetic product (1,2-product), and the thermodynamic product (1,4-product) are observed to be predominant at lower and higher temperatures, respectively.

Because the 1,4-product is more stable than the 1,2-product, the 1,4-product is the major thermodynamically controlled product. Consequently, after the reaction takes place, there would be an equilibrium state between the two products. Conversion from the 1,2-product to the 1,4-product has an activation energy of 313.07 kJ/mol, and the reverse conversion requires 328.79 kJ/mol of energy. The activation energy from the 1,2-product was slightly less than that from the 1,4-product. This means that it is easier to convert the 1,2-product to the 1,4-product than in the reverse direction because it takes less energy to obtain the more stable product. This is the reason why the thermodynamic product becomes the major product over time.

By analyzing the reaction in terms of kinetics, $k_{1,2}/k_{1,4}$ ratio was calculated at various temperatures using the Arrhenius equation. Increasing temperature decreased the ratio significantly meaning that as temperature increased, 1,4-addition became more favorable. Since this ratio is proportional to [1,2-product]/[1,4-product], increasing temperature increases the yield of the thermodynamically controlled product. Increasing the temperature provides more energy so that the activation energy gap could be overcome to give the more stable product. By thermodynamically analyzing this reaction, $K_{1,2}/K_{1,4}$ ratio (proportional to the ratio of 1,2 product yield to that of 1,4 product) was calculated at varying temperatures. As temperature was increased, this ratio increased very slightly because $K_{1,4}$ decreases at a faster rate than $K_{1,2}$ (both paths are exothermic, but the 1,4-addition reaction is more exothermic so temperature causes a greater effect on this reaction than the 1,2-addition reaction). However, the thermodynamic ratio is hardly affected by temperature and the variation is negligible.

Combining the two ratios predicts the relative yield of both products taking into account both kinetic and thermodynamic affects. At 193 K (-80°C), the combined ratio favors 1,4-product formation by 1.6 times meaning that computational analysis predicts a 63.3% 1,4-product yield and 36.7% 1,2-product yield. At 298.15 K (25°C), the prediction is 85.5% 1,4-product and 14.5% 1,2-product yields. And 318 K (45°C), it is 87.1% 1,4-product and 12.9% 1,2-product yields. These results show that as temperature increases, the thermodynamically more stable product becomes predominant. These trends in the relative product yields agree well with the trend seen in experimental results although the actual yields predicted are different. The major reason for the weakness in predicting the actual yields computationally is that while the computational data is obtained for the gas phase reaction, the experimental product yields are obtained in liquid solution. Presence of solvent molecules changes the amount of kinetic energy available for the reactant molecules significantly besides imparting solvation effects to reaction energy. Also one of the reactants of this reaction, HBr, is partially ionized in organic solvent whereas it is in molecular form in the gas phase. The computations in this study did not take into account the ionized form of HBr which would affect the energy calculations of the reaction pathway. Correcting for these effects would definitely change the outcome of the yields so that computational and experimental results could agree not only in trend, but also numerically with one another.

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