

Organohalide Nucleophilic Substitution Transition State Analysis with Hydroxide Anion

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Abstract

We consider the S_N2 reaction of haloethanes and hydroxide anion in an attempt to find the transition state in the General Atomic Molecular and Electronic Structure System (GAMESS) program. In transition states involving fluorine to bromine Møller–Plesset perturbation theory of the second order (MP2) and Pople style basis set 3-21G(d,p) showed to give the best performance. Becke exchange functionals showed large favoring towards products and were very unresponsive to transition states.

Keywords

Transition states, Methods, Basis Sets, Substitution Reactions, Halides, GAMESS, Pseudopotentials, Density functional Theory, Perturbation Theory

1. Introduction

The transition state is an important part of a chemical reaction since it can both give insight into the reaction mechanism of a reaction and the energy of the state can be used to calculate the activation energy of the reaction. While it is simple to identify a transition state of a simple chemical reaction on paper, it is an arduous task to do so in computational chemistry—specifically in the General Atomic Molecular and Electronic Structure System (GAMESS) program. This study attempted to find the transition states for the S_N2 reaction of haloethanes, from fluoroethane to iodoethane, with a hydroxide anion using GAMESS(US).

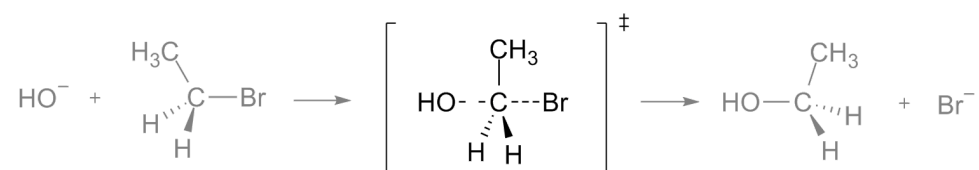


Figure 1. S_N2 reaction of bromoethane with a hydroxide anion¹

2. Method

2.1 Initial Geometry

The determination of a transition state was studied from the approach suggested by Xuefei Xu et. al.² The build of the structure was done initially in the molecular modeling software Avogadro.³

2.1 Optimization/Selecting a Basis and Method

The initial geometry was optimized using the Møller–Plesset perturbation theory of the second order(MP2)⁴ with the Pople style doubly split valence basis set 3-21G(d,p).⁵ This combination was at the discretion of Xuefei et. al.² The basis 6-31G(d,p) was described as giving good results, 3-21G(d,p) was found to provide a better system in our case.² Becke exchange type functionals proved to be some of the worst to use in our system as they, in all scenarios, formed the product.

2.2 Frequencies

The frequencies of the optimized geometry were studied using MP2/3-21G. Additionally, density functional theory(DFT) using the Slater Exchange functional⁶ with the one-Parameter Progressive correlation^{7,8} (SOP) combination with Huzinaga's 21 split valence basis set⁹ was used to calculate the frequencies of said optimized geometry. The oxygen carbon(1) coordinate was fixed to a predetermined value in order for the frequency to complete. These frequencies will act as the initial reaction coordinate used to find our saddle point energy for the transition state.

2.3 Saddle Point Energies

The method and basis set chosen for the calculation of the frequencies of the optimized geometry were used to calculate the saddle point energies of the system. The transition state was considered when the mode of vibration matched our reaction coordinate found previously from the frequencies. The acceptance of a transition state involved how linear along the O-C1-X coordinate the structure was, the distance of the bond lengths, the interactions between all the atoms and the presence of a singular imaginary frequency.

3. Results and Discussion

3.1. Molecular Orientation

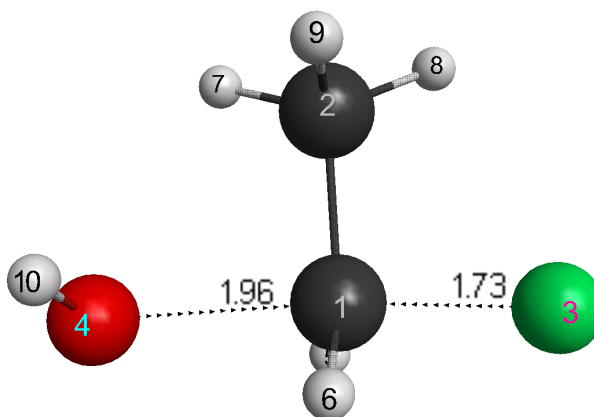


Figure 2. Fluoroethane transition state geometry and length between hydroxide and chloride with respect to C1 in angstroms with MP2/3-21G method and basis set. Produced in MacMolPlt.¹⁰

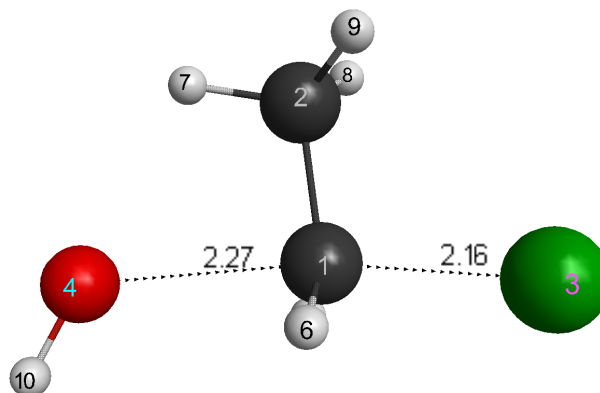


Figure 3. Chloroethane transition state geometry and length between hydroxide and chloride with respect to C1 in angstroms with MP2/3-21G method and basis set. Produced in MacMolPlt.¹⁰

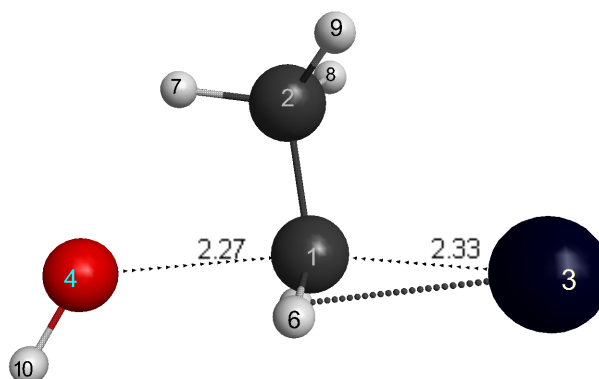


Figure 4. Bromoethane transition state geometry and length between hydroxide and chloride with respect to C1 in angstroms with MP2/3-21G method and basis set. Produced in MacMolPlt.¹⁰

3.2. Analysis of Data

Halide (MP2/3-21G)	X-C Bond Length(Å)	HO-C Bond Length(Å)	Transition State Mode of Vibration(cm^{-1})
F	1.73	1.96	-532.36
Cl	2.16	2.27	-430.13
Br	2.33	2.27	-437.28

Table 1. X-C and HO-C bond lengths and transition state mode of vibration for ethyl halides with MP2/3-21G method and basis set.

Halide (SOP/MIDI)	X-C Bond Length(Å)	HO-C Bond Length(Å)	Transition State Mode of Vibration(cm^{-1})
F	1.75	2.0	-420.77
Cl	2.21	2.36	-610.18
Br	2.21	2.39	-173.54

Table 2. X-C and HO-C bond lengths and transition state mode of vibration for ethyl halides with SOP/MIDI method and basis set.

3.3 Discussion

MP2/3-21G method and basis set proved to be proficient in locating our predicted reaction coordinate. Furthermore, the SOP/MIDI method and basis set also provided a predicted reaction coordinate. However, the transition state using the MP2/3-21G method provided less interactions between the atoms not taking part in the transition. Moreover, SOP/MIDI had a tendency to shift the hydroxyl group “into” the page decreasing the wanted linearity of our transition state along the O-C1-X coordinate. Fluorine proved to be the simplest atom to study, which followed a general trend of increased difficulty in convergence within the Hartree Fock SCF iterations and with the saddle point calculations the heavier the atom studied was. The MP2/3-21G method and basis set also out performed the SOP/MIDI combination in computation time by roughly half the time in every system. The MP2 method was not able to converge when used with the MIDI basis. Similar to MP2 and MIDI, the SOP method was not able to converge with the 3-21G basis set. This discrepancy may not allow us to accurately compare both types of calculations, but shows that more than one methodology gives valuable results.

The bond lengths between the hydroxide and carbon 1 are the same for both Br and Cl with the MP2/3-21G method and basis set as seen in Table 1. The bond lengths being equivalent in both cases suggests that the hydroxide is unaffected by the species of halide after fluorine. However, successful transition state calculations for iodine and astatine should be completed to confirm the claim.

The abnormally low mode of vibration for bromine using the SOP/MIDI calculation can be attributed to the bromine not being a part of the supported atoms of the MIDI basis set. When calculating

for the transition state GAMESS did not signal an error and allowed the calculation to run. What GAMESS used for the basis of bromine is unknown.

Xuefei et. al. had found that M08-HX and M06-2X methods were found to perform the best, these calculations were done with the MG3S basis set.² M08-HX and M06-2X were not able to give a transition state when we performed the calculations. This could be attributed to our change of basis set to 3-31G(d,p). The MG3S basis has an equivalent basis of 311G(2p) for lighter atoms to 6-311+G(3d2f) for heavier atoms.¹¹ This basis had 2 major problems for our study: the first being that the equivalent larger basis was previously tested and showed poor results, and the second being that MG3S only goes to argon not allowing us to study bromine.¹¹ For the sake of comparison we have decided to try and use only one basis per method. Furthermore, we were not able to corroborate the effectiveness of M08-HX and M06-2X as methods for transition states (using 3-21G(d,p) and MIDI basis sets). Although these methods did provide a decrease in time compared to the SOP method the saddle point energy was not able to be found.

4. Iodine

Effectiveness of a basis set was a continual challenge in this study. The larger the basis the more the system moved to produce the product, ethanol. This, alongside the recommendation by Xuefei et. al. to use a smaller basis set for MP2 were the reasons 3-21G(d,p) was used. However, aug-cc-pVDZ and def2-SVP, although “larger” basis sets, showed promise. Both basis sets calculated a linear structure but could not complete the saddle point energy calculation. A pseudopotential was used in order to reduce the significant time increase that the relatively large iodine atom would require. Using the same methods as the other halogens, iodine was not able to work with the ECP supported basis sets: SBKJC Polarized (p,2d)-LFC, def2-SVP, and aug-cc-pVDZ. Triple zeta set basis proved to be “too much” for the system and would not properly run. The optimization and hessian was able to be performed and gave promising results as seen below.

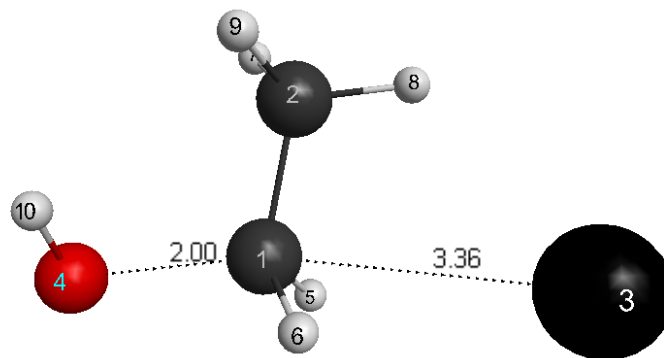


Figure 5. Iodoethane transition state geometry and length between hydroxide and chloride with respect to C1 in angstroms with MP2/3-21G method and basis set. Produced in MacMolPlt.¹⁰

5. Conclusion

The purpose of this study was to find the transition states for the S_N2 reaction of haloethanes. Transition states of fluorine to bromine were able to be found using the MP2/3-21G(d,p) method and minimal basis set with much efficiency. The same systems were studied using the SOP/MIDI DFT method and minimal basis set. The DFT calculations showed less favorable results in a greater time. Cancellation of errors allows the smaller basis sets to give better results compared to the larger ones; 3-21G(d,p) proved to be the most stable and accurate basis set.

Acknowledgements

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