



Theoretical Investigation of the SN2 Reaction Mechanism from Methyl Chloride to Methyl Fluoride Using Density Functional Theory

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(Received: 16 September 2024

Revised: 11 October 2024

Accepted: 11 December 2024)

KEYWORDS

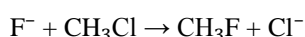
SN2 Reaction ,
Methyl Chloride,
Methyl Fluoride

ABSTRACT:

This report presents a theoretical investigation of the bimolecular nucleophilic substitution (SN2) reaction mechanism, where fluoride ion (F⁻) displaces the chloride ion (Cl⁻) in methyl chloride (CH₃Cl) to form methyl fluoride (CH₃F). Density Functional Theory (DFT) calculations were employed to elucidate the reaction pathway, characterize the transition state, and determine the activation energy. The study provides insights into the electronic structure and energetics of the reaction, contributing to a deeper understanding of SN2 mechanisms in organic chemistry.

1. Introduction

The SN2 reaction is a fundamental mechanism in organic chemistry, characterized by a single, concerted step where a nucleophile attacks an electrophilic carbon, leading to the simultaneous displacement of a leaving group. In this study, we focus on the reaction between fluoride ion and methyl chloride:



Understanding the mechanistic details of this reaction is essential, as it serves as a model for nucleophilic substitutions involving alkyl halides.

2. Computational Methods

All calculations were performed using the ORCA software package. The B3LYP functional was employed in conjunction with the Def2-TZVP basis set for all atoms. Solvent effects were modelled using the

Polarizable Continuum Model (PCM) with water as the solvent. Nudge elastic band (NEB) method has been used for the transition state calculation. The transition state (TS) for the reaction was located and confirmed by the presence of a single imaginary frequency. Geometry optimizations were carried out for the reactants, products, and transition state, followed by frequency calculations to confirm the nature of each stationary point.

3. Results and Discussion

3.1. Reactants and Products

The optimized geometries of the reactants (F⁻ and CH₃Cl) and the product (CH₃F) were obtained. The C–Cl bond length in CH₃Cl was found to be 1.811 Å, while the C–F bond length in CH₃F was 1.411 Å, consistent with experimental data.

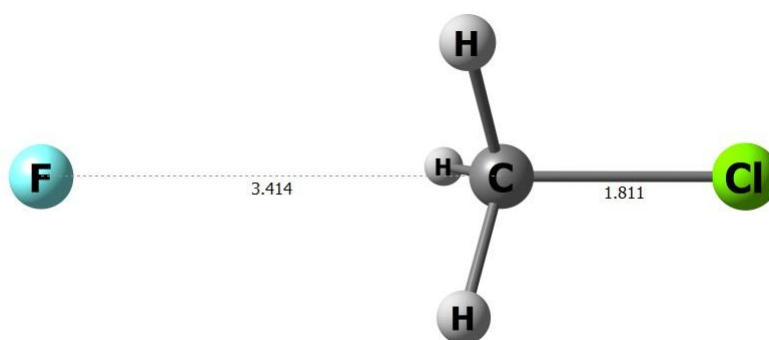


Fig.1 – Optimized geometry of reactants

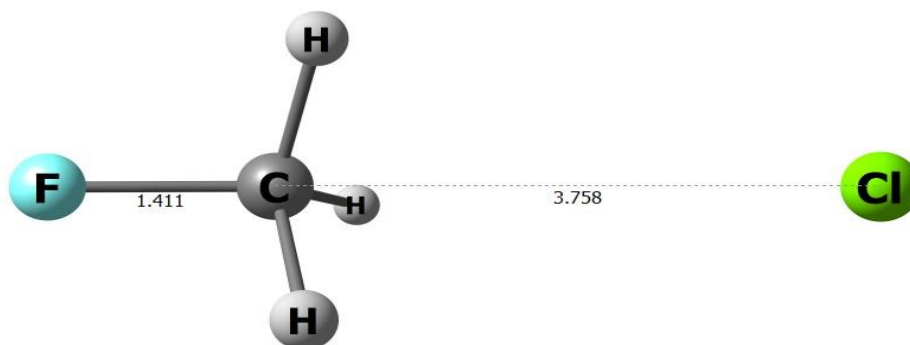


Fig. 2 – Optimized geometry of products

3.2. Transition State

The transition state (TS) for the reaction was located and confirmed by the presence of a single imaginary frequency at -475.64 cm^{-1} corresponding to the

nucleophilic attack and simultaneous leaving group departure. In the TS, the C–Cl and C–F bond lengths were 2.232 Å and 1.999 Å , respectively, indicating a symmetric, pentacoordinate carbon atom.

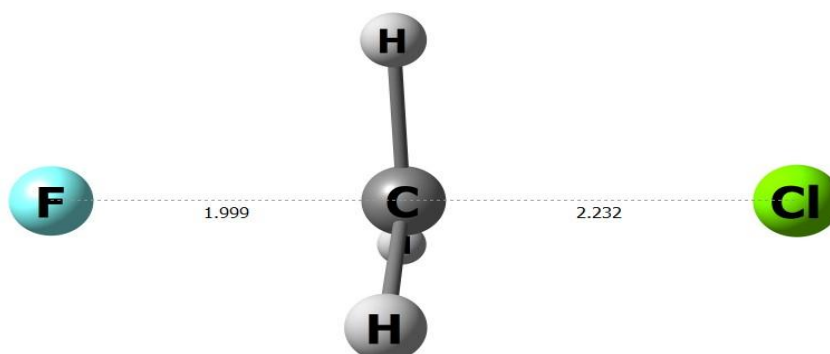


Fig. 3 – Geometry of Transition State

3.3. Activation Energy

The activation energy (ΔE^\ddagger) for the reaction was calculated as the energy difference between the

transition state and the reactants. In the gas phase, ΔE^\ddagger was found to be 11.6 kcal/mol . Table 1 shows the total energy calculated using DFT at B3LYP level and Def2-TZVP basis set.

Table 1: Total energies of various systems using b3lyp/def2-TZVP

S.No.	System	Total Energy (Hartree)	Total Energy (eV)
1	Reactant ($\text{F}^- + \text{CH}_3\text{Cl}$)	-600.0482	-16328.152
2	Transition State ($\text{CH}_3\text{F}-\text{Cl}^-$)	-600.02967	-16327.647
3	Product ($\text{CH}_3\text{F} + \text{Cl}^-$)	-600.06984	-16328.74

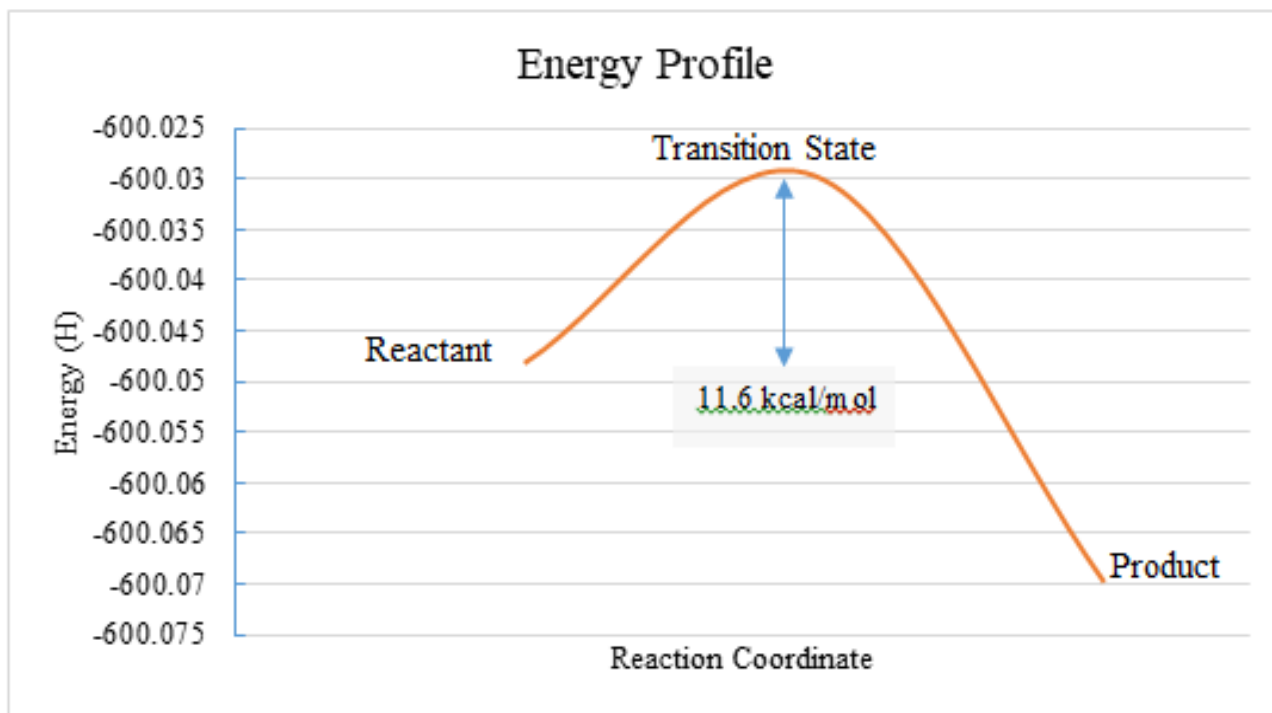


Fig 4: Reaction coordinate

3.4. Reaction Mechanism

The calculated data support a concerted SN₂ mechanism with a backside attack by the fluoride ion, leading to inversion of configuration at the carbon center. The transition state is characterized by a planar arrangement of the carbon and the two halogen atoms, with partial bonds to both the incoming nucleophile and the leaving group.

4. Conclusion

This theoretical investigation provides a detailed understanding of the SN₂ reaction mechanism between fluoride ion and methyl chloride. The DFT calculations reveal that the reaction proceeds via a single transition state with an activation energy of 11.6 kcal/mol. These findings are consistent with the classical description of SN₂ reactions and offer quantitative insights into the energetics and structural characteristics of the process.

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