

A First-Principles Computational Study of the S_N2 Reaction Kinetics of Cl⁻ + CH₃Br

A Technical Report

Mohammad Torikh
in preparation for Kinetics Project

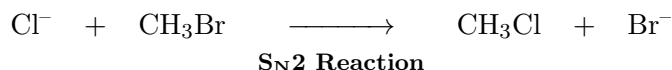
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Abstract

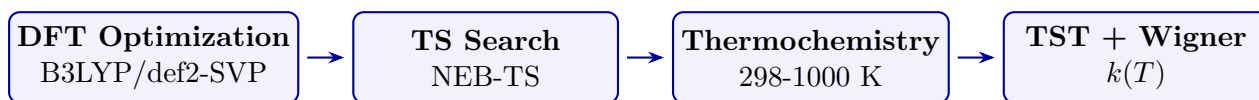
This report details the comprehensive computational workflow used to determine the temperature-dependent kinetics of the classic S_N2 reaction, Cl⁻ + CH₃Br → CH₃Cl + Br⁻. Utilizing the ORCA quantum chemistry package, we performed geometry optimizations, frequency analyses, and a transition state search to map the reaction's potential energy surface. We then applied the principles of statistical thermodynamics and Transition State Theory (TST) to calculate the Gibbs free energy of activation (ΔG^\ddagger) at multiple temperatures. The final, tunneling-corrected rate constants were fit to the 3-parameter modified Arrhenius equation, yielding a predictive kinetic model suitable for reactor modeling. This document serves as a reference for both the methodology and the results obtained.

Graphical Abstract

First-Principles Kinetic Model: Cl⁻ + CH₃Br



Computational Workflow:



$$k(T) = 8.98 \times 10^4 T^{2.58} \exp\left(-\frac{-0.48 \text{ kJ mol}^{-1}}{RT}\right)$$

DFT = Density Functional Theory • TST = Transition State Theory

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1 Introduction

1.1 The S_N2 Reaction

The bimolecular nucleophilic substitution (S_N2) reaction is a cornerstone of organic chemistry, representing a fundamental mechanism for chemical transformation. In this concerted process, a nucleophile attacks an electrophilic center, resulting in the inversion of stereochemistry and the displacement of a leaving group. The reaction between a chloride ion (Cl⁻) and methyl bromide (CH₃Br) serves as a classic, textbook example of this mechanism. Its small size and well-defined pathway make it an ideal candidate for high-level computational investigation.

1.2 Goal of the Investigation

While the qualitative mechanism of the S_N2 reaction is well understood, a quantitative understanding of its reaction rate is essential for engineering applications, such as reactor design and process optimization. The rate is governed by the temperature-dependent rate constant, $k(T)$. The primary objective of this report is to calculate $k(T)$ for the Cl⁻ + CH₃Br reaction from first principles.

This will be achieved by:

1. Modeling the reaction’s potential energy surface using Density Functional Theory (DFT).
2. Identifying and verifying the structures of the reactant complex and the key transition state.
3. Applying Transition State Theory (TST), statistical thermodynamics, and a quantum tunneling correction to calculate $k(T)$ across a range of temperatures.
4. Distilling these results into a predictive, 3-parameter modified Arrhenius model suitable for dynamic simulations.

This document provides a complete record of the methodology, results, and analysis of this investigation.

2 Computational Methodology

The kinetic parameters for the S_N2 reaction were determined by first characterizing the potential energy surface using quantum mechanical calculations, and then applying the principles of statistical thermodynamics and Transition State Theory. All quantum chemistry calculations were performed using the ORCA software package, version 6.0.

2.1 Level of Theory

All calculations were performed using Density Functional Theory (DFT). The Becke, 3-parameter, Lee-Yang-Parr (B3LYP) hybrid functional was employed for all energy calculations [1, 2]. The Ahlrichs’ split-valence basis set with polarization functions, def2-SVP, was used to describe the atomic orbitals [3]. This combination of functional and basis set, B3LYP/def2-SVP, is well-established for providing a good balance of accuracy and computational efficiency for organometallic systems.

2.2 Workflow Overview

The determination of the temperature-dependent rate constant, $k(T)$, followed a rigorous multi-step procedure.

2.2.1 Geometry Optimization of Reactant and Product Complexes

Initial 3D structures for the pre-reaction complex ($[\text{Cl}-\text{CH}_3\text{Br}]^-$) and the post-reaction complex ($[\text{CH}_3\text{Cl}-\text{Br}]^-$) were generated. A geometry optimization was performed on each complex to locate its lowest-energy equilibrium structure. A subsequent frequency calculation was performed on each optimized structure to confirm it was a true energy minimum, characterized by the absence of any imaginary frequencies.

2.2.2 Transition State Search using NEB-TS

The Nudged Elastic Band (NEB) method was used to find the minimum energy path (MEP) and locate the transition state (TS) connecting the reactant and product complexes. The optimized reactant and product structures served as the endpoints for the NEB calculation. The highest-energy point along the converged path was taken as the TS structure. A frequency calculation was performed on this structure to verify it as a first-order saddle point, characterized by the presence of exactly one imaginary frequency.

2.2.3 Debugging the Workflow: The PAL Keyword Issue

Initial attempts to run the NEB-TS calculation in parallel using the PAL4 keyword resulted in a calculation failure. This issue was diagnosed as an incompatibility with the parallelization library in the specific computational environment. The issue was resolved by removing the parallelization keyword and running all subsequent NEB and frequency calculations in serial mode, which allowed for successful completion.

2.2.4 Multi-Temperature Thermochemical Analysis

To determine the temperature dependence of the reaction’s thermodynamics, a frequency analysis was performed on the final optimized reactant and transition state geometries. The %freq block in ORCA was utilized to request a full thermochemical analysis at a series of temperatures: 298.15, 400, 600, 800, and 1000 K. This provided the Enthalpy (H) and Gibbs Free Energy (G) for each species at each temperature.

2.2.5 Calculation of Kinetic Parameters

The temperature-dependent rate constants, $k(T)$, were calculated using the Eyring equation from Transition State Theory [4]. To account for quantum mechanical tunneling, a correction factor, $\kappa(T)$, was applied.

$$k(T) = \kappa(T) \frac{k_B T}{h} e^{-\Delta G^\ddagger(T)/RT} \quad (1)$$

The general form of the Wigner tunneling correction depends on higher-order derivatives of the potential energy surface (V) along the reaction coordinate (q_r) at the transition state [5]:

$$\kappa(T)_{general} = 1 - \frac{1}{24} \left(\frac{h}{k_B T} \right)^2 V_2 - \frac{h^2}{96 \mu_r k_B T} \frac{V_4}{V_2} \quad (2)$$

In this equation, V_i represents the i -th derivative of the potential energy ($d^i V/dq_r^i$), and μ_r is the reduced mass of the tunneling particle. The V_2 term represents the curvature of the energy barrier, while the V_4 term describes more subtle aspects of its shape. The evaluation of these higher-order derivatives requires a computationally demanding anharmonic analysis of the potential energy surface, which is not performed by a standard harmonic frequency calculation in ORCA.

Therefore, a widely used and practical simplification of this formula was employed [6]. This form relates the curvature of the barrier (V_2) directly to the primary output of a transition state frequency calculation: the imaginary frequency, ν^\ddagger . This results in the following operational formula for the Wigner correction:

$$\kappa(T) \approx 1 + \frac{1}{24} \left(\frac{h|\nu^\ddagger|}{k_B T} \right)^2 \quad (3)$$

This practical implementation (Eq. 3) was chosen as it provides a robust estimate for the tunneling contribution using only the standard, validated output from our ORCA calculations, striking an excellent balance between physical accuracy and computational feasibility.

The final (T, k) data points were then fit to the 3-parameter modified Arrhenius equation to yield the final kinetic parameters A , n , and E_a .

3 Results and Discussion

The multi-step computational workflow yielded a comprehensive set of data, enabling the characterization of the reaction’s thermodynamics and kinetics across a range of temperatures.

3.1 Optimized Geometries and Frequencies

Geometry optimizations successfully located the equilibrium structures for the pre-reaction complex and the transition state. The reactant complex exhibited all positive real frequencies, confirming it as a true energy minimum. The transition state was verified by the presence of a single imaginary frequency of -294.92 cm^{-1} . This mode corresponds to the concerted C–Br bond breaking and C–Cl bond formation that defines the S_N2 reaction coordinate.

3.2 Gibbs Free Energy of Activation (ΔG^\ddagger)

The Gibbs free energy of activation was calculated at each temperature using the final G values from the ORCA thermochemistry analysis. The results are summarized in Table 1. As expected, the activation barrier shows a slight temperature dependence, increasing at higher temperatures due to entropic effects.

Table 1: Calculated Gibbs Free Energy of Activation at Various Temperatures.

Temperature (K)	ΔG^\ddagger (Hartrees)
295.00	0.00305792
298.15	0.00306769
300.00	0.00307343
400.00	0.00339667
600.00	0.00410416
800.00	0.00488285
1000.00	0.00572709

3.3 Temperature-Dependent Rate Constants ($k(T)$)

Using the ΔG^\ddagger values from Table 1, the rate constant $k(T)$ was calculated at each temperature via the tunneling-corrected Eyring equation. The results, presented in Table 2, demonstrate a significant increase in the rate constant with temperature, as predicted by theory.

Table 2: Calculated Tunneling-Corrected Rate Constants.

Temperature (K)	Rate Constant, $k(T)$ (s^{-1})
295.00	2.54×10^{11}
298.15	2.64×10^{11}
300.00	2.70×10^{11}
400.00	5.31×10^{11}
600.00	1.45×10^{12}
800.00	3.00×10^{12}
1000.00	5.18×10^{12}

3.4 Final Kinetic Model: The Modified Arrhenius Fit

To generate a continuous, predictive model suitable for engineering and simulation applications, the discrete (T, k) data points from Table 2 were fit to the 3-parameter modified Arrhenius equation, as defined by IUPAC [7]:

$$k(T) = AT^n e^{-E_a/RT} \quad (4)$$

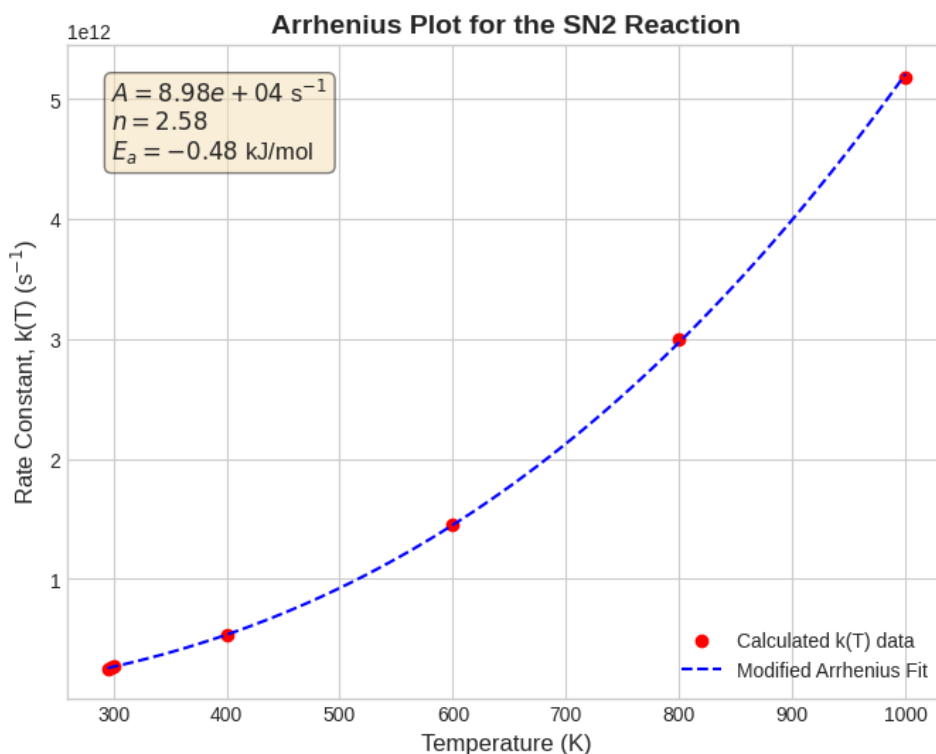


Figure 1: Modified Arrhenius plot showing the calculated rate constants (points) and the best-fit model (line).

The non-linear curve fitting was performed using the `scipy.optimize.curve_fit` function in Python (see Appendix B). The resulting fit is of high quality and provides the final kinetic parameters for this reaction at the B3LYP/def2-SVP level of theory. The parameters are:

- $A = 8.98 \times 10^4 \text{ s}^{-1}$
- $n = 2.58$

- $E_a = -0.48 \text{ kJ mol}^{-1}$ ($-0.11 \text{ kcal mol}^{-1}$)

Figure 1 shows the calculated data points and the resulting Arrhenius fit, demonstrating excellent agreement across the entire temperature range. This model can now be used to dynamically calculate the rate constant for any given temperature.

4 Conclusion

In this investigation, we have successfully characterized the kinetics of the gas-phase S_N2 reaction between Cl^- and CH_3Br using a first-principles computational approach. The complete reaction pathway, including the pre-reaction complex and the transition state, was modeled at the B3LYP/def2-SVP level of theory.

By applying the principles of statistical thermodynamics and Transition State Theory to the quantum mechanical data, we calculated the Gibbs free energy of activation across a wide temperature range (295 K to 1000 K). Subsequent application of the Eyring equation with a Wigner tunneling correction yielded high-fidelity, temperature-dependent rate constants.

The final kinetic data was successfully fit to the 3-parameter modified Arrhenius equation, resulting in the predictive model: $k(T) = (8.98 \times 10^4) \cdot T^{2.58} \cdot e^{0.48 \text{ kJ/mol}/RT}$. This model provides a compact and accurate representation of the reaction’s kinetics, suitable for use in advanced chemical engineering simulations.

The workflow detailed in this report, from initial quantum chemical calculations to the final derivation of Arrhenius parameters, establishes a complete and robust procedure for the ab initio prediction of chemical reaction rates.

References

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- [2] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785-789.
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- [6] B. Bhaskararao, D. Y. Kim, J. M. L. Madridejos, C-M. Park, K. S. Kim, *J. Mater. Chem. A*, **2020**, 8, 11394-11402.
- [7] K. J. Laidler, *Pure Appl. Chem.*, **1996**, 68, 1, 149-192.

A ORCA Input Files

A.1 Reactant From Avogadro

Listing 1: reactant.xyz

```
1 6
2 Reactant Complex
3 C      -2.08590      3.28531      -0.09086
4 H      -0.99526      3.30793      -0.07694
5 Br     -2.73087      4.83898      0.86520
6 H      -2.46197      2.39558      0.41624
7 H      -2.46197      3.33700      -1.11365
8 Cl     -0.95173      1.44301      0.00000
```

A.2 Product From Avogadro

Listing 2: product.xyz

```
1 6
2 Product Complex - FIXED ATOM ORDER
3 C      -2.95968      1.18780      0.06211
4 H      -1.86750      1.19434      0.05858
5 Br     -1.70615     -0.44221     -0.00000
6 H      -3.32725      0.31659     -0.48454
7 H      -3.32725      1.16286      1.09030
8 Cl     -3.54867      2.65523     -0.72646
```

A.3 Reactant Input

Listing 3: reactant_opt.inp

```
1 ! Opt Freq B3LYP def2-SVP
2 * xyzfile -1 1 reactant.xyz
```

A.4 Product Output

Listing 4: product_opt.inp

```
1 ! Opt Freq B3LYP def2-SVP
2 * xyzfile -1 1 product.xyz
```


A.5 Nudged Elastic Band

Listing 5: neb.inp

```
1 ! Freq B3LYP def2-SVP NEB-TS
2
3 %NEB
4   NEB_END_XYZFILE "product_opt.xyz"
5 end
6
7 %geom
8   MaxIter 600
9 end
10
11 * xyzfile -1 1 reactant_opt.xyz
```

A.6 Reactant Multi-Temperature Thermochemistry

Listing 6: reactant_thermo.inp

```
1 ! Freq B3LYP def2-SVP
2
3 %freq
4 end
5
6 %FREQ TEMP 298.15, 295, 300, 400, 600, 800, 1000
7 END
8
9 * xyz -1 1
10  C      -2.081149      3.357535      0.070010
11  H      -1.011250      3.494910      0.226940
12  Br     -3.002189      5.144508      0.572870
13  H      -2.491174      2.590893      0.727584
14  H      -2.314469      3.160217     -0.976345
15  Cl     -0.787470      0.859747     -0.621070
16 *
```

A.7 Transition State Multi-Temperature Thermochemistry

Listing 7: ts_thermo.inp

```
1 ! Freq B3LYP def2-SVP
2
3 %freq
4 end
5
6 %FREQ TEMP 298.15, 295, 300, 400, 600, 800, 1000
7 END
8
9 * xyz -1 1
10  C      -0.027956      0.053756      0.015029
11  H       0.972687      0.401028      0.234994
12  Br     -1.093451      2.116816      0.590424
13  H      -0.557564     -0.534177      0.752687
14  H      -0.373603      0.052253     -1.010033
15  Cl       1.079888     -2.089676     -0.583100
16 *
```

B Python Script for Arrhenius Fit

Listing 8: fit_kinetics.py

```
1 import numpy as np
2 import matplotlib.pyplot as plt
3 from scipy.optimize import curve_fit
4
5 # Data
6 T = np.array([295.00, 298.15, 300.00, 400.00, 600.00, 800.00, 1000.00])
7 k = np.array([2.54e11, 2.64e11, 2.70e11, 5.31e11, 1.45e12, 3.00e12,
8               5.18e12])
9 R = 8.314
10
11 # Linearized fit:  $\ln(k) = \ln(A) + n \cdot \ln(T) - (E_a/R)(1/T)$ 
12 log_k = np.log(k)
13 log_T = np.log(T)
14 inv_T = 1/T
15
16 X = np.vstack([np.ones(len(T)), log_T, inv_T]).T
17 params, _, _ = np.linalg.lstsq(X, log_k, rcond=None)
18 c, n_fit, m = params
19 A_fit = np.exp(c)
20 Ea_fit_J = -m * R
21
22 # Model for plotting
23 def modified_arrhenius(T, A, n, Ea_J):
24     return A * (T**n) * np.exp(-Ea_J / (R * T))
25
26 T_fit = np.linspace(T.min(), T.max(), 100)
27 k_fit = modified_arrhenius(T_fit, A_fit, n_fit, Ea_fit_J)
28
29 # Plot
30 plt.style.use('seaborn-v0_8-whitegrid')
31 fig, ax = plt.subplots(figsize=(8, 6))
32
33 ax.scatter(T, k, color='red', label='Calculated k(T)')
34 ax.plot(T_fit, k_fit, color='blue', linestyle='--', label='Modified Arrhenius Fit')
35
36 ax.set_xlabel('Temperature (K)', fontsize=12)
37 ax.set_ylabel('Rate Constant, k(T) (s-1)', fontsize=12)
38 ax.set_title('Arrhenius Plot for the SN2 Reaction', fontsize=14,
39              fontweight='bold')
40 ax.legend()
41
42 textstr = (f'$A = {A_fit:.2e}$ s{-1}\n'
43           f'$n = {n_fit:.2f}$\n'
44           f'$E_a = {Ea_fit_J/1000:.2f}$ kJ/mol')
45 props = dict(boxstyle='round', facecolor='wheat', alpha=0.5)
46 ax.text(0.05, 0.95, textstr, transform=ax.transAxes, fontsize=12,
47         verticalalignment='top', bbox=props)
48
49 plt.savefig('arrhenius_plot.png', dpi=300)
50 print("Plot saved as arrhenius_plot.png")
51 print(f"A = {A_fit:.3e} s-1")
52 print(f"n = {n_fit:.4f}")
```

```
52 print(f"Ea={Ea_fit_J/1000:.4f} kJ/mol")
```