Electronic and thermodynamic properties during phenol to salicylic acid conversion

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Abstract

The phenol to salicylic acid conversion (PTSC), also known as the Kolbe-Schmitt reaction, this reaction is very important for food preservatives and the pharmaceutical industry. Phenol reacts with sodium hydroxide to form sodium phenoxide, then carboxylates with carbon dioxide at 125°C and 100 atm to yield salicylic acid. Despite multiple research studies, mechanistic details, catalyst influences, and electronic structures remain unexplored. This study employs the use of Density Functional Theory (DFT) with B3LYP/def2-TZVP and Coupled Cluster CCSD(T) methods using ORCA software to investigate reaction pathways, transition states, and electronic properties. Geometries have been optimised with strict SCF convergence, and vibrational analyses used to confirm minima. This study provides insights into bond lengths, angles, IR spectra, and orbital distributions improve understanding of aromatic reactivity and thermodynamics, bridging experimental gaps for industrial applications.

Keywords: Kolbe-Schmitt reaction, Density Functional Theory (DFT), Salicylic acid, Phenol, Quantum chemistry

Introduction

This project was done through the Undergraduate Research Opportunities Scheme (UROS) by the University of Lincoln. The aim of the scheme is to provide necessary first-hand experience with working on a research project alongside an academic mentor during their studies. This project has achieved this by engaging and supporting the student to meaningfully contribute to all the stages of the research process, including literature research, computational setup and methodology, data analysis, and

write-up of article and poster. This project examined the phenol to salicylic acid conversion (PTSC), also known as the Kolbe-Schmitt reaction, using computational methods such as DFT. The study explores the reaction pathway, transition states, and electronic properties to provide insights into this industrially important transformation of phenol to salicylic acid.

Project Background

Phenol to salicylic acid conversion (PTSC) is an important process in the food and pharmaceutical industries. It is used to keep food fresh and as a step in making aspirin. The first step in this well-studied process is to turn phenol into sodium phenoxide with sodium hydroxide. Then, at a high temperature (125 °C) and pressure (100 atm), it is carboxylated with CO2 to make salicylic acid. This process shows how simple organic molecules like phenol can be changed to make a wide range of compounds that can be used for many things. This study is driven by the necessity to attain a more profound comprehension of its electronic structure, catalytic influences, and mechanistic intricacies, which remain inadequately elucidated despite extensive prior investigation into the framework. As an undergraduate studying chemistry, this subject corresponds with my interest in computational methodologies for organic reactions and the potential to expand into the investigation of catalytic processes. It directly pertains to my research in quantum chemistry and organic synthesis, where experimental constraints impede comprehensive understanding. This project seeks to close this gap by using computer tools and models to show how the electronic distribution in the aromatic ring and substituents changes over time. This can elucidate experimental reactivity trends. Ultimately, the research direction centres on employing Density Functional Theory (DFT) in conjunction with Coupled Cluster CCSD(T) to simulate the pathway, thereby yielding essential insights for the Kolbe-Schmitt process.

Literature Review

The Kolbe-Schmitt reaction has been studied experimentally for optimising yields and conditions, but computational insights into the mechanism, thermodynamics, and electronic structure are minimal. Initial studies focused more on the practical aspects of the reaction. Kolbe (1860) initially proposed the direct carboxylation of sodium phenoxide, while Schmitt (1885) improved yields by preventing phenol volatilisation, leading to its industrial uses. Studies by Lindsey and Jeskey (1957) reviewed variations in carbonation of phenols, temperature, pressure, and the substituent effects on regioselectivity. However, there were mechanistic debates regarding intermediates. Theoretical studies on the quantum chemistry of the reaction emerged: Marković et al. (2003) used DFT to model the gas-phase mechanism, revealing four steps involving three transition states and intermediates, starting with a PhONa-CO2 complex and ending in a 1,3-proton shift to salicylate. Solvent effects were explored by Stanescu

and Achenie (2006), showing that solvents influence kinetics by stabilising intermediates, with the potential to make the final step reversible and reduce the yields. Marković et al. (2007) further examined the potassium phenoxide-CO2 complex structure, emphasising metal ion roles in coordination. Recent reviews by Wu et al. (2023) disprove traditional views, proposing carbonate complexes as actual intermediates that can rearrange, which was supported by IR and NMR data. Themes include solvent impacts (e.g., gas-solid vs. solution phases), catalyst influences (e.g., alkali metals), and electronic factors affecting ortho-selectivity. However, with all the growing research, gaps remain in the comprehensive thermodynamics of intermediates, which computational chemistry can address beyond experimental limits.

Methodology

For my research, I aimed at understanding the mechanistic pathway, location of transition states, and electronic properties in the Kolbe-Schmitt reaction. My strategy is appropriate in literature because it offers measurable bond lengths, angles, and orbitals, which are not feasible in experimental literature. The ORCA program was employed in carrying out quantum chemistry calculations based on DFT theory. Furthermore, the B3LYP functional was applied in calculating the geometries of reactants, while the def2-TZVP basis set was employed in carrying out geometry optimisation. Finally, harmonic frequency calculations were done, enabling the determination of whether optimised geometries were indeed real stationary points, without imaginary frequencies in support. To obtain important details such as geometrical, electronic, and vibrational conditions (IR), files were analysed. To obtain credible SCF, calculations were done under extremely stringent conditions, including an energy tolerance of 1.0×10^{-9}Eh, orbital, and orbital rotation limits. These conditions were appropriate in ensuring that optimised geometries converged accurately, making it feasible in the literature. Single-point energy calculations were done in Coupled Cluster theory based on optimised geometries from DFT, in line with best practices in literature (Marković et al., 2003).

Results

Information was gathered through computational simulations using the ORCA software package, employing Density Functional Theory (DFT) with the B3LYP functional and def2-TZVP basis set. Geometries of reactants, intermediates, and products were optimised, followed by harmonic vibrational frequency calculations to confirm minima (no imaginary frequencies). Infrared (IR) spectra, bond lengths, angles, Mulliken bond orders, and energetics (ΔH and ΔG) were computed from output files.

Qualitative results validated the method via IR spectra benchmarking. For phenol, DFT peaks at ~756 and 696 cm^{-1} (C6H5 bending), 1192 cm^{-1} (C-O stretch), 3183 cm^{-1} (aromatic C-H), and 3798 cm^{-1} (O-H stretch) closely matched experimental values at

~750 and 690, 1192, 3090, and 3621 cm^{-1} (NIST Office of Data and Informatics, 1966). Salicylic acid showed a broad O-H stretch at ~3166 cm^{-1} (exp. ~3278 cm^{-1}) and C=O at ~1760 cm^{-1}, with aromatic vibrations at 1645, 1510, and 1487 cm^{-1}, aligning well with literature (NIST Office of Data and Informatics, 1959). See Figure 2 for spectra.

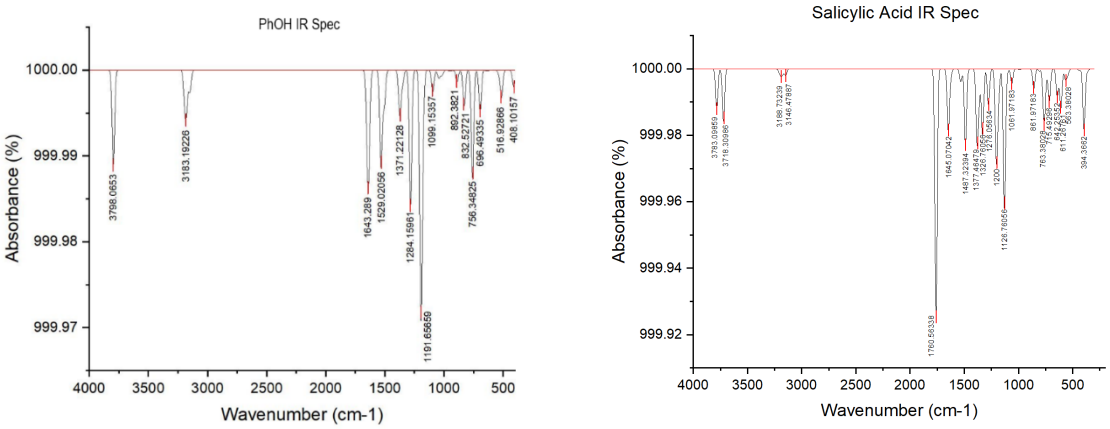

Figure 2: IR Spectrum of Phenol and Salicylic Acid produced by the Orca Code.

The reaction mechanism involves five elementary steps (Figure 3). Quantitative geometrical changes:
The enthalpy of each of the elementary reactions was calculated using equations (1) and (2) shown below:

$\Delta H_{reaction} = \Delta H_{product} - \Delta H_{reactant}$ [1]

where, $H = E_{el} + ZPE + H_{thermal}$ [2]

Here, $\Delta H_{product}$ and $\Delta H_{reactant}$ are the changes in enthalpy for the products and reactants. These values give us the $\Delta H_{reaction}$ when used in equation 1, which describes the total change in energy of the reaction.
H is the Enthalpy, where E_{el} is the Electronic Energy, ZPE is the Zero-Point Energy, and $H_{Thermal}$ is the thermal enthalpy of the reactant or product. Equation 2 is important in the production of the necessary values to find the $\Delta H_{reaction}$.
The reaction energy (ΔG) was calculated using

$\Delta G = G_{React} - G_{Prod}$. [3]

Here, G_{React} and G_{Prod} are the Gibbs free energy for the reactant and products respectively.

Step 1 (deprotonation) - O-H bond breaks from 1.040 Å; O-Na forms at 2.080 Å; C-O shortens from 1.342 to 1.316 Å; C-O-Na angle ~160° vs. C-O-H 113.3°; ΔH = -8.78 kJ/mol (exothermic). Step 2 (carboxylation) - C5-C4 elongates to 1.497 Å; new C4-C7 bond 1.561 Å; CO2 bends with C-O ~1.26 Å; Mulliken bond order for C3-O1 = 2.013; ΔH = +242.71 kJ/mol (endothermic). Step 3 (protonation/rearrangement) - C1-C2 shortens to 1.463 Å; carboxyl C7-O2 = 1.208 Å (double, bond order 2.076), C7-O1 = 1.339 Å (single, 1.268); O1-H5 = 0.971 Å (H-bond); ΔH = +8.02 kJ/mol. Step 4 - C1-O3 = 1.356 Å; O3-H7 = 0.962 Å; C6-C7 = 1.499 Å; Mulliken C1-O3 order drops from

2.174 to 1.305; ΔH = +6.85 kJ/mol. Step 5 (alternative) - Similar geometry to Step 4; C7-O2 = 1.220 Å, C7-O1 = 1.351 Å; Mulliken C1-O3 from 2.036 to 1.245; ΔH = -134.38 kJ/mol (exothermic, but less favourable pathway).
Overall ΔH = +114.42 kJ/mol (net endothermic). These findings support the project's hypothesis that computational analysis would reveal mechanistic details, electronic changes, and thermodynamic drivers, confirming Step 2 as rate-determining and Ste

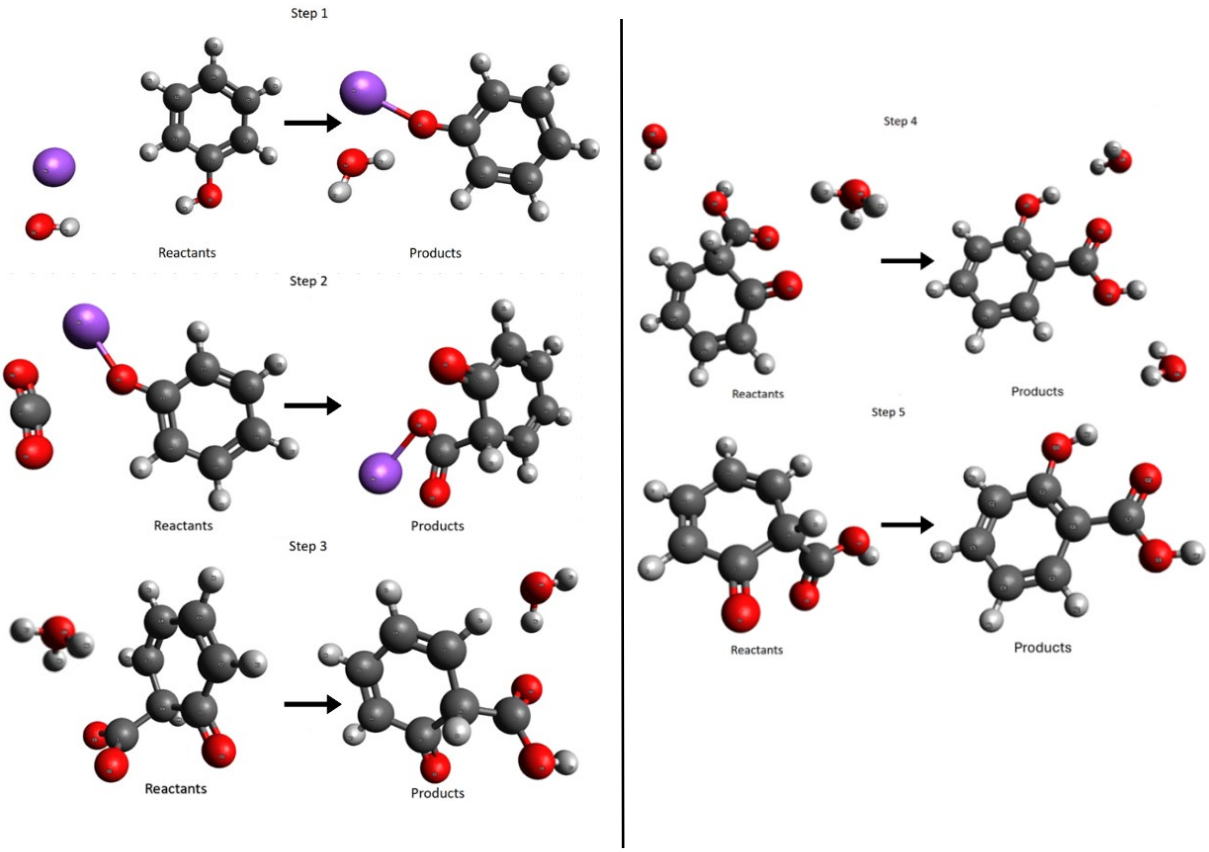

Figure 3: A reaction map of all elementary steps involved within the conversion of Phenol to Salicylic Acid

UROS Experience

Involvement in the Undergraduate Research Opportunities Scheme (UROS) has been an extremely rewarding experience, which has enabled me to participate in research that surpasses regular coursework. Currently, I am an undergraduate in chemistry at the University of Lincoln, and this project concerning the conversion of phenol to salicylic acid has aligned ideally with my interests in computational quantum chemistry and served as a means to initiate study into catalysis. I undertook all aspects of the research, ranging from literary reviews that indicate a gap in knowledge concerning

the mechanism to implementation of calculations in ORCA and production of the final report under the guidance of my supervisor, which has given me hands-on experience in using computational methods such as B3LYP and CCSD(T).

Conclusion

In this work, we studied the conversion of phenol to salicylic acid by using DFT. The results showed good agreement of calculated IR peaks with literature values, confirming the reliability of the method. This was followed by a detailed analysis of the geometrical properties and energetics of the reactants and products for each of the elementary steps. Geometrical analysis of each intermediate showed mostly planar aromatic cores, but great local changes at the oxygen atoms and carboxyl group formation. The thermodynamics proved that step 2 (carboxylation) was the most endothermic and essentially drove the reaction forward, while step 5 was shown to be exothermic and not favourable in terms of the pathway. Step 4 was identified as the favourable final reaction path, giving a stable –COOH group and leading directly to the formation of salicylic acid. For future work, we will perform the Nudge Elastic Band method calculations to investigate the energy barriers in both gas and solvent phases and also test the mechanism of this reaction on surfaces. We also plan to use higher levels of theory to further improve the accuracy of the energetics of pathway description.

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