

Kinetic study of order of reaction and mechanics investigation of the oxidation of isoborneol by trichloroisocyanuric acid in acidic medium

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Abstract. This paper examines the kinetic and mechanism of the oxidation of isoborneol which is a bicyclic secondary alcohol, using trichloroisocyanuric acid (TCCA) in acidic solution. The reaction was studied in a systematic manner by changing the concentrations of the substrate, oxidant, and hydrogen ions as well as temperature. The kinetic data show that the reaction is dependent on isoborneol and TCCA in the first order. The fact that the reaction rate increases with greater acidity implies the involvement of protonated oxidizing species. The product of the oxidation was found to be camphor establishing the conversion of the secondary alcohol into a ketone. On the basis of the experimental observations, a plausible mechanism that takes hypochlorous acid as the active oxidizing species has been forwarded. The considered activation parameters also confirm the suggested mechanistic pathway.

1. Introduction

One of the most fundamental and broadly studied changes in organic chemistry is the oxidation of alcohols to their respective carbonyl counterparts. This conversion is very important both in laboratory level synthesis and in large scale industrial processes especially in synthesis of pharmaceutical, agrochemicals, fragrance and fine chemicals. The process of converting secondary alcohols to ketones is of particular importance in the light of the versatility and reactivity of the derived carbonyl products as intermediates in a wide range of synthesis processes. Bicyclic alcohols like isoborneol, in this respect received a lot of interest due to its level of structural complexity and industrial value. Isoborneol is a naturally occurring terpene alcohol that is a precursor of camphor, which is used widely in medicinal preparations, applied topically, as a plasticizer and in aromatic preparations. It is of acidic and commercial importance therefore that the selective and efficient oxidation of isoborneol to camphor occurs.[1]

Over the last few years, the importance of the creation of effective, selective, and environmentally friendly oxidizing agents has grown. Of these, the trichloroisocyanuric acid (TCCA) has been found to be a promising reagent because of its large oxidative capacity, economical nature, ease of handling, and comparatively low environmental health repercussions in comparison to the conventional chromium-based oxidants. TCCA is a solid, stable compound that can be easily stored and transported and, therefore, it was very suitable in terms of practical use. In acidic solutions, TCCA hydrolyzes to produce reactive oxidation species like hypochlorous acid (HOCl) and their protonated forms (e.g., H_2OCl^+). Under some conditions, it can also produce molecular chlorine. These species are also known to be actively involved in oxidation reactions, enabling the oxidation of alcohols to carbonyl derivatives along either the electrophilic or hydro generation routes.[2]



Even though the literature has reported oxidation of different primary and secondary alcohols with TCCA, there is a relative paucity of kinetic and mechanistic investigations on bicyclic systems, especially on isoborneol. A majority of the current literature has concentrated on simpler aliphatic or aromatic alcohols and there is yet to be a gap in comprehending the reactivity patterns of stricter sterically hindered and structurally rigid substrates such as isoborneol. Stereochemistry and ring strain peculiar to bicyclic systems can play a significant role in the reaction pathway, rate and mechanism. Thus, the kinetics and mechanism of isoborneol oxidation requires a closer study to have a better understanding of these systems.[3]

It is against this consideration that the current project is being conducted so that the kinetics of oxidation of isoborneol by TCCA in acidic medium can be analyzed systematically. The purpose of the work is to establish the order of reaction in respect to different reactants, to examine the influence of reaction parameters on the reaction e.g. acidity and temperature as well as to suggest a plausible reaction mechanism that is consistent with the experimental observations. This type of study does not only help in advancing the core knowledge on the process of oxidation, but also gives me helpful information on improving the reaction conditions under practical application.[4]

2. Experimental

2.1 Materials

All the chemicals/reagents used in the current research were of analytical reagent (AR) grade and were not purified further. Isoborneol was obtained in high purity and its identity was checked before usage. The oxidizing agent (trichloroisocyanuric acid, TCCA) was recently prepared or standardized prior to every group of experiments to make sure that there was accuracy in concentration.

The medium was aqueous acetic acid, which was prepared by the combination of glacial acetic acid as well as distilled water in the right proportions to obtain the desired composition in the solvent. The acidic conditions that were required during the reaction were maintained with hydrochloric acid. All solutions were prepared with the double-distilled water. Standard sodium thiosulfate solution was made and standardised to iodometric titrations and potassium iodide and starch indicator was excessively added to ensure full reaction during the analysis.

All the glassware that was used in the experiments was properly washed, rinsed with distilled water and dried before use to prevent contamination and reproducibility of the obtained results.

2.2 Kinetic Measurements

Under pseudo-first-order conditions, the kinetic experiment was conducted by keeping the amount of isoborneol that is in excess compared to TCCA, such that the amount of isoborneol was actually constant throughout the reaction process. The reactions were carried out in a water bath that had been thermostatically controlled to ensure that the temperature remained stable (± 0.1 K).[6]

It was reacted by the addition of known volume of pre-equilibrated solution of TCCA with the reaction mixture of isoborneol, acetic acid, and hydrochloric acid. All the experiments were done in the same volume of reaction. Aliquots of the reaction mixture were sampled at preset time intervals and quenched instantly in potassium iodide solution at iced conditions to stop the further reaction.

The leftover level of TCCA was established iodometrically by titration of the discharged iodine over regular sodium thiosulfate solution utilizing the starch as an indicator. The loss of the blue colour indicated the end of the titration. The rate constants were determined using the linear plots of the logarithm of concentration against time and the results proved that the dependency was first-order with regard to TCCA.

2.3 Product Analysis

At the end of the course of the reaction, the reaction mixture was exposed to product isolation measures. The organic solvent was used to extract the organic product and then it was purified through conventional methods like recrystallization or distillation.

Purification of the product was done by analysing the physical and spectral characteristics of its product. The literature values were compared to the melting point of the isolated compound which was measured and used to identify it. In order to verify the existence of specific functional groups, infrared (IR) spectroscopy was used. A bright absorption band at the carbonyl C=O stretching vibration was observed which is a good indication of formation of camphor.[7]

The overall analytical data made the conclusive decision that isoborneol oxidizes to produce camphor as the major product, hence the anticipated conversion of a secondary alcohol to a ketone under the specified conditions of the experiment.

3. Results and Discussion

3.1 Stoichiometry of the Reaction

The stoichiometry of oxidation of isoborneol by trichloroisocyanuric acid (TCCA) was determined through conducting experiments using different initial concentration of reactants but letting the reaction to go to completion. Their findings show that a single mole of isoborneol reacts with a single mole of TCCA forming a 1:1 stoichiometric ratio between the oxidant and the substrate.[8]



This stoichiometric correlation proves that TCCA is a good oxidizing reagent and it catalysed the oxidation of the secondary alcoholic group of isoborneol to a ketonic functional group. The fact that the major oxidation product is camphor also lends this conclusion. Figure 1 demonstrates the total oxidation of isoborneol to camphor.

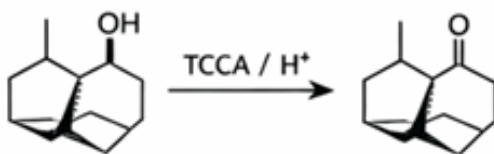


Figure 1 Oxidation of Is borneol to Camphor by TCCA in Acidic Medium

3.2 Kinetic Order

Kinetic studies were conducted with the reaction through varying the concentration of TCCA and isoborneol separately keeping the rest of the experimental conditions unaltered. There was integrated rate equations used in the analysis of the rate data.

The dependence of the reaction on TCCA was of first order, as seen in the linear appearance of plots of logarithm of residual oxidant concentration versus time. In the same way, the proportional dependence of the rate of the reaction on the variation of the isoborneol concentration also indicated a first order dependence of the reaction on isoborneol. First-order kinetics are established by the fact that the linear plot of $\ln [\text{TCCA}]$ vs. time (Figure 2) confirms first-order.[9]

Accordingly, the overall rate law for the reaction can be expressed as:

$$\text{Rate} = k[\text{Isoborneol}][\text{TCCA}]$$

where k represents the second-order rate constant. The observed kinetic order suggests that both the substrate and oxidant participate directly in the rate-determining step of the reaction. [figure 3]

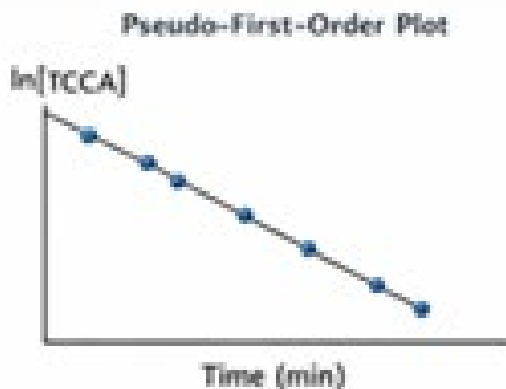


Figure 2 Pseudo First-Order Plot

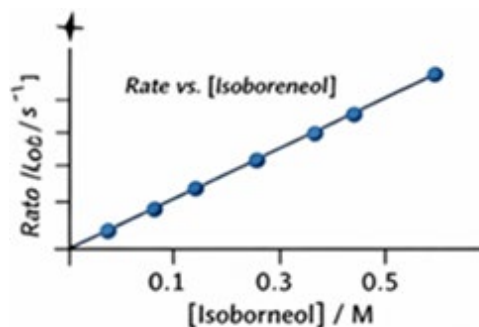


Figure 2 Effect of Is borneol Concentration

3.3 Effect of Hydrogen Ion Concentration

The rate of the reaction in the presence of hydrogen ion was studied as the concentration of hydrochloric acid was varied holding other variables under a constant condition. The findings illustrate that reaction rate increased significantly with greater acidity of the medium.[10]

Such a behaviour reflects that the oxidation is catalysed by hydrogen ions. It is possible to mention the increase rate caused by protonation of hypochlorous acid (HOCl) resulting in formation of the more reactive electrophilic species like H_2OCl^+ . This protonated form has a higher oxidizing potential and has a more effective interaction with the substrate. [11,12]. Thus, the dependence of reaction rate on acid concentration provides strong evidence for the involvement of protonated oxidizing species in the reaction mechanism [fig 4].

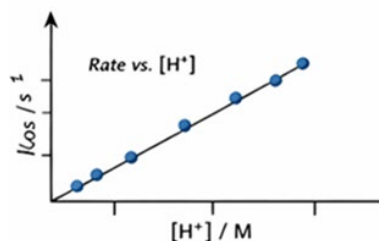


Figure 4 Effect of Hydrogen Ion Concentration

3.4 Effect of Temperature

The effect of temperature on the oxidation reaction was studied over a suitable temperature range under otherwise identical conditions. The rate of reaction was found to increase significantly with increasing temperature, consistent with the Arrhenius equation.

A plot of $\ln k$ versus $1/T$ yielded a straight line, confirming the validity of Arrhenius behavior. From the slope and intercept of the plot, the activation energy (E_a) and other thermodynamic parameters such as the entropy of activation (ΔS) and enthalpy of activation (ΔH) were calculated.

The activation energy was found to be moderate, indicating that the reaction proceeds at a reasonable rate under experimental conditions. The negative value of entropy of activation suggests the formation of a more ordered transition state, possibly due to the association between the substrate and the oxidizing species during the rate-determining step.[Figure 5]

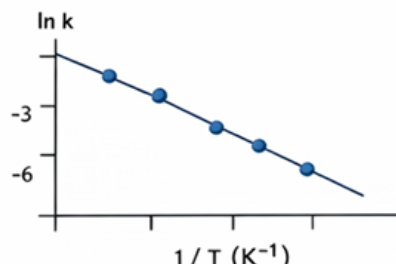


Figure 5 Arrhenius Plot

3.5 Proposed Reaction Mechanism

Based on the experimental observations and kinetic data, a plausible mechanism for the oxidation of isoborneol by TCCA in acidic medium is proposed.

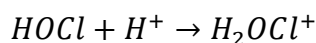
Step 1: Generation of Active Oxidizing Species

In acidic aqueous medium, TCCA undergoes hydrolysis to generate hypochlorous acid:



Step 2: Protonation of Hypochlorous Acid

The hypochlorous acid formed is further protonated in the presence of excess hydrogen ions:



Step 3: Formation of Intermediate Complex

The protonated oxidizing species interacts with isoborneol to form an intermediate complex. This step involves the approach of the oxidizing species towards the hydroxyl-bearing carbon atom of the substrate.

Step 4: Hydride Transfer and Oxidation

A hydride ion is transferred from the substrate to the oxidizing species, leading to the formation of a carbocation-like transition state, which subsequently rearranges to form the ketone.

Step 5: Product Formation

The intermediate decomposes to yield camphor as the final oxidation product along with reduced forms of the oxidant.[Figure 6]

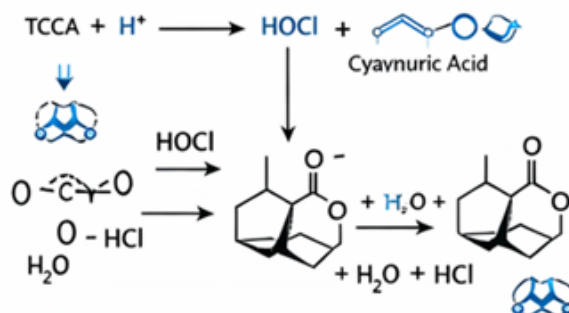


Figure 6 Proposed Reaction Mechanism

3.6 Mechanistic Interpretation

- The proposed mechanism is in good agreement with the experimental findings and successfully explains the observed kinetic behavior:
- The first-order dependence on both isoborneol and TCCA indicates that both species are involved in the rate-determining step.
- The increase in rate with hydrogen ion concentration supports the involvement of protonated oxidizing species such as H_2OCl^+ .
- The negative entropy of activation suggests the formation of a highly ordered transition state, consistent with the formation of an intermediate complex.
- The formation of camphor confirms the oxidation of the secondary alcohol group to a ketone.
- Overall, the mechanism provides a coherent explanation for the kinetics and product distribution observed in the oxidation of isoborneol by TCCA in acidic medium.

4. Conclusion

Isoborneol is oxidized by trichloroisocyanuric acid in acidic media following a clear kinetic pathway with a first-order dependence on both reactants. The reaction occurs with the help of protonated oxidizing species produced on the spot. The oxidation of the secondary alcohol group is proven by the formation of camphor. The experimental kinetic data and thermodynamic parameters are in good agreement with the proposed mechanism.

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