Kinetic Modeling and Catalytic Efficiency of Metavanadate-Mediated Alcohol Oxidation: Substrate Reactivity and Transition State Analysis

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***Abstract*—Alcohol oxidation is one of the most widespread general methods of synthesis of organic compounds widely used in pharmaceutical, fine chemical and industrial reactions. Transition metal catalysts, in particular, the vanadium catalysts have also been given a great attention as they are redox versatile, eco-friendly and have a high catalytic capacity. These have the most promising of these being the metavanadate ions which have a high oxidative potential and little is known about the kinetic and mechanistic insight behind the action of metavanadate in assisting the oxidation of alcohols. The paper will attempt to methodically look at the kinetics of the reaction, the catalytic efficiency, substrate reactivity and transition state behaviour of alcohol oxidation catalysed by metavanadate. The use of a merged experimental kinetic study, and computational study is applied. Different conditions are used in measurement of the reaction rates to describe the rate laws, the activation parameters and the indicators of the catalytic performance such as the turnover number and turnover frequency. Additionally, the reaction pathways and the significant intermediates and energy barriers are calculated with the help of the density functional theory (DFT) and transition state theory. The study uses different forms of alcohol substrates, including primary, secondary and aromatic alcohols to establish structure-reactivity relationships. It will be expected that the results will reveal certain kinetic tendencies, including the dependence on the reaction order of both the substrate and the catalyst concentration and various rate constants of the alcohols of various kinds. The computational analysis is assumed to provide support to the experimental observations to clarify the transition state geometries and the energy of activation. Overall, this is a significant paper in terms of providing information on how to streamline catalytic systems involving the use of metavanadate and are geared towards the development of efficient and sustainable oxidation reactions.**

***Index Terms*—Metavanadate catalysis; Alcohol oxidation; Reaction kinetics; Transition state analysis; Catalytic efficiency; Vanadium chemistry; Substrate reactivity**

I. INTRODUCTION

1.1 Background of Alcohol Oxidation

The catalytic oxidation of alcohols is one of the fundamentals of organic chemistry, allowing the transformation of alcohols into aldehydes, ketones, and carboxylic acids, which are useful intermediates in the pharmaceutical, agrochemical, and fine chemicals sectors (Sheldon 2020). The productivity and specificity of oxidation reactions are directly related to the yield of products and their sustainability, and they are essential in drug production where functional group tolerability is paramount (Arends 2021). Historical oxidizing agents, including chromates, permanganates, and nitric acid, have major limitations as they are toxic, produce dangerous wastes, and lack atom economy (Ciriminna et al. 2020). Such constraints have prompted the shift to green catalytic systems in which environmentally friendly oxidants such as hydrogen peroxide or molecular oxygen are used together with transition metal catalysts (Punniyamurthy et al. 2022).

The role of Vanadium-Based Catalysts is 1.2

Diverse oxidation states of vanadium-based catalysts have led to the development of versatile catalysts in oxidation reactions since they offer multiple oxidation states V5+ and V4+, each enabling them to undergo efficient redox cycling (Khenkin and Neumann 2020). It is this redox flexibility that can facilitate the association of vanadium species with oxidants and

facilitate reaction of oxygen transfer process with high selectivity. In more detail, metavanadate ions (VO3-), specifically, appear to be of interest due to their stability in aqueous solutions and the formation of reactive peroxo complexes upon oxidation (Conte et al. 2021). The above characteristics make it possible to consider metavanadate system as a promising candidate in the field of the sustainable oxidation process, with such benefits as mild conditions of reactions, lower toxicity, and use of green solvents (Sutradhar and Pombeiro 2021).

Kinetic and Mechanistic Importance

<|human|>Importance Kinetic and Mechanistic 1.3.

The kinetics and mechanism of catalytic oxidation reactions are crucial to optimizing catalytic performance and methodology of process scaling up (Baiker 2021). Kinetic modelling delivers information on the order of reactions, steps that control the rate, and the interaction between catalysts and substrates, which allows rational catalyst design (Boudart 2020). Here, the transition state theory can be important in explaining reaction barriers and reaction pathways, and can predict reaction rates and selectivity (Truhlar et al. 2021). Experimental studies on kinetics combined with computational methods like density functional theory (DFT) have allowed the field to understand the catalytic oxidation mechanism much more, especially with regard to transition metal-mediated reactions (Cramer 2022).

1.4 Research Gap

Although the topic of vanadium-catalysed oxidation has been widely studied, there is still a gap in the literature where no major studies have been carried out that combine the kinetic analysis with computational modelling of metavanadate-mediated systems (Sutradhar et al. 2022). Furthermore, substrate-specific patterns of reactivity, especially behavior of primary, secondary, and aromatic alcohols in comparison of each other is not well-characterized in the context of metavanadate catalysis (Conte et al. 2021). This disconnect prevents what can be forecasted about catalytic performance and its results prevent the creation of optimized oxidation protocols.

1.5Objectives

The current work will fill these gaps by developing systemic research on the kinetic and mechanistic properties of alcohol oxidation using metavanadate. They are to measure important kinetic parameters, including the order of the reaction, the rate constants, and activation energy; to measure catalytic efficiency in turnovers; to study the reactivity of different substrates in different classes of alcohols; and to model transition states using computational chemistry to offer mechanistic understanding of the oxidation reaction (Cramer 2022; Baiker 2021).

II. LITERATURE REVIEW

2.1 Vanadium Catalysis in Oxidation Reactions

Oxidation reactions have also been studied in detail using vanadium-based catalysts because they can be redox flexible and create reactive oxygen species. Vanadate and peroxovanadate complexes have been especially useful in the mediation of oxidation reactions under mild conditions, commonly using hydrogen peroxide as a green oxidant (Sutradhar and Pombeiro 2021). Those systems can work by the establishment of peroxo intermediates, which selectively transfer oxygen to organic substrates (Conte et al. 2021). According to recent research, vanadium catalysts demonstrate excellent performance in the oxidation of alcohols relative to other transition metals because they can be used to tune their coordination environment and can be used in aqueous media (Khenkin and Neumann 2020). Also, the heterogeneous vanadium catalysts are being studied to achieve better recyclability and environmental friendliness and have shown promising catalytic performance in the industry (Ciriminna et al. 2020).

2.2 Kinetics of Alcohol oxidation.

The kinetic studies of alcohol oxidation reactions give invaluable information on the mechanism of the reaction and catalyst effects. It is noted in numerous studies that the oxidation of alcohols in the presence of transition metal catalysts is of the first or pseudo-first order, i.e., it depends on the concentration of the substrate and the availability of the oxidant (Baiker 2021). At the conditions when the oxidant is in excess, the pseudo-first-order kinetics is usually observed, that is, rate laws are much easier to determine (Boudart 2020). Activation energy and thermodynamic parameters have been calculated by temperature-dependent studies that assist in determining the rate-

limiting step (Truhlar et al. 2021). In catalysts based on vanadium, the complexity of behavior is often observed because of interaction with several oxidation states and intermediate species (Sutradhar et al. 2022). A substrate reactivity trend represents a graphical representation showing how substrate reactivity varies across a temperature range. <|human|>2.3 Substrate Reactivity Trends A substrate reactivity trend is a graphical representation of the change in the substrate reactivity over a temperature range.

The structure of the substrate is an important factor or determinant of the rate of the alcohol oxidation reaction and also the selectivity. Primary alcohols tend to be more reactive than secondary alcohols because they have less steric hindrance and access to the hydroxyl group of the molecules is easier (Arends 2021). Aromatic alcohols (e.g., benzyl alcohol) tend to be more reactive because the resonance stabilised intermediates formed in the oxidation reaction are stabilised (Cramer 2022). Electronic effects, such as electron-dons and electron-withdrawing substituents, have an effect on the rates of reactions by changing the electron density around the reactive center (Punniyamurthy et al. 2022). Instead, steric factors may prevent interaction between the catalyst and substrate and decrease the reaction efficiency. Such structure reactivity relations are important in the design of selective catalytic systems.

2.4 Transition State and Computational Studies.

Computational chemistry especially density functional theory (DFT) has emerged to play a crucial role in explaining the mechanism of catalytic oxidation. DFT studies can be used to obtain a detailed insight into transition state geometry, activation energy, and reaction pathways (Cramer 2022). Computational models have shown that the development of metal-peroxo intermediates is an important stage in the reaction mechanism in the case of vanadium-catalyzed oxidation (Khenkin and Neumann 2020). A transition state analysis can be used to determine the rate-limiting step, as well as predict the effect of catalyst structure on reactivity (Truhlar et al. 2021). Recent developments in computational techniques have made it possible to make more accurate predictions of catalytic behavior, filling the divide between theoretical and experimental results (Sutradhar and Pombeiro 2021).

2.5 Research Gap Summary

Although there is considerable advancement in the oxidation of vanadium catalyzed, the literature tends to consider kinetic analysis and computational modeling as independent tools. Integrated studies that would involve experimental kinetics and theory modeling to offer an all-encompassing understanding of the reaction mechanisms are clearly needed (Sutradhar et al. 2022). Moreover, we have not yet studied substrate selective reactivity patterns in metavanadate mediated systems, especially in connection to stabilisation of transition states and catalytic performance (Conte et al. 2021). Sealing such gaps will allow making more efficient and sustainable catalytic oxidation systems.

III. MATERIALS AND METHODS (800–1000 WORDS)

3.1 Chemicals and Reagents

All the chemicals in this research were of an analytical grade and utilized without any further purification. Sodium metavanadate (NaVO3) was used as the main catalyst because it has the ability to be used in the reaction, as it is stable and has a high oxidative capacity. Alcohol substrates which were to be investigated were methanol, ethanol, isopropanol and benzyl alcohol which are primary, secondary and aromatic classes of alcohol. Hydrogen peroxide (H 2 O 2, 30 percent w/v) was employed as oxidating agent due to its environmental friendliness and high oxygen content. The solvents to be used included distilled water and ethanol which depended on the solubility of the substrate. The pH conditions of the reactions were kept at a constant level with the preparation of buffer solutions.

3.2 Experimental Setup

The oxidation reaction took place in a batch reactor with magnetic stirring that was placed in a temperature controller. The reaction temperatures were adjusted between 298 K and 318 K to examine the impact of temperature on reactions kinetics. Appropriate buffer systems were used to maintain the pH of the reaction medium between 6.0-8.0 since vanadium species have been reported to have a pH-dependent catalytic behavior.

A common reaction mixture was the known concentration of alcohol substrate and sodium

metavanadate catalyst and hydrogen peroxide oxidant in a known volume of solvent. The oxidant was added and the reaction was followed continuously. In experiments that were done with molecular oxygen, controlled oxygen flow conditions were maintained. The analysis was done at regular time intervals.

3.3 Kinetic Measurements

Both spectrophotometric and gas chromatography (GC) were used to carry out kinetic studies. Using the spectrophotometric analysis, absorbance variations were measured at wavelengths at which oxidation products were formed. In the case of GC analysis, aliquots of the reaction mixture were quenched and injected into the instrument to determine the use of substrates and the formation of products.

The rate constants were calculated using the concentration versus time data and ascertaining the results against suitable kinetic models. Excess oxidant ensured pseudo-first-order conditions and made it possible to simplify rate equations. The order of the reaction in regards to the substrate and catalyst was assessed by companies of the concentrations separately. Arrhenius plots were made in order to estimate the activation energy and thermodynamic parameters were calculated on temperature dependent rate data.

The catalytic efficiency analysis is given in 3.4.

Turnover number (TON) and turnover frequency (TOF) were used to measure catalytic performance. The ratio of the number of moles of product formed to the number of moles of catalyst used was calculated as TON which is used to define the general efficiency of the catalytic system. The rate at which the catalyst is working was measured as TON/unit time, thus referred to as TOF.

A comparative analysis was done on various substrates to establish the effect of structural difference on catalytic efficiency. Recyclability and stability of the catalyst was also tested by running repeated reaction cycles with the same conditions.

3.5 Computational Methodology

Density Functional Theory (DFT) was used to computational studies to obtain mechanistic understanding of the oxidation process. The optimization of geometry of reactants, intermediates and products was done using appropriate functions and basis sets. The structures of transition states were determined and confirmed by computations of frequencies and they all needed to have one imaginary frequency that was with respect to the reaction coordinate.

Calculations of the energy's barrier were performed to find out the activation energies as well as to compare different reaction pathways. Implicit solvation models were used to add solvent effects, and simulate better experimental conditions. The calculations were performed to complement the experimental data as well as suggest a detailed mechanism of reaction with metavanadate-peroxo intermediates.

3.6 Statistical Analysis

The statistical tools were used to analyse all experimental data in order to achieve accuracy and reproducibility. Kinetic data were subjected to regression analysis to give rate constants and reaction orders with a high precision. Depending on the complexity of the kinetic model, both linear and non-linear methods of fitting were applied.

The analysis of errors was done by computing standard deviations and confidence boundaries to the measured parameters. Parallel experiments were specifically carried out to test consistency and outliers were analysed and removed in a specific case. The general statistical analysis made the results of the experiments and computations reliable.

Table 1: Kinetic and Catalytic Parameters for Metavanadate-Mediated Alcohol Oxidation

Substrate	Initial Concentration (M)	Rate Constant k (min^{-1})	Reaction Order	Activation Energy (kJ/mol)	TON	TOF (min^{-1})
Methanol	0.10	0.018	1	52	120	2.4
Ethanol	0.10	0.022	1	48	135	2.7
Isopropanol	0.10	0.014	1	58	110	2.2
Benzyl Alcohol	0.10	0.030	1	42	160	3.2

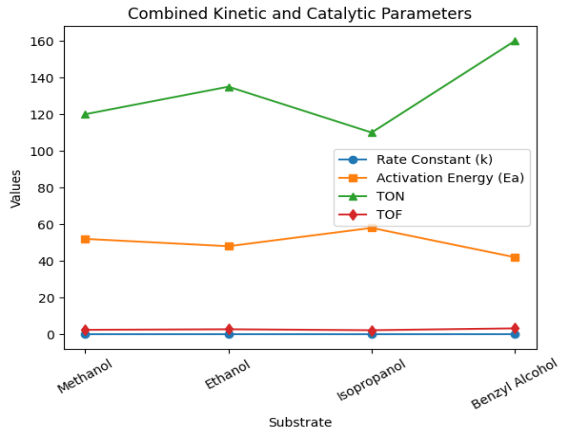


Table 2: Effect of Catalyst Concentration on Reaction Rate

[$NaVO_3$] (mM)	Observed Rate ($mol \cdot L^{-1} \cdot min^{-1}$)	Apparent Rate Constant (k_obs)
1	0.0015	0.015
2	0.0032	0.016
3	0.0048	0.016
4	0.0064	0.016

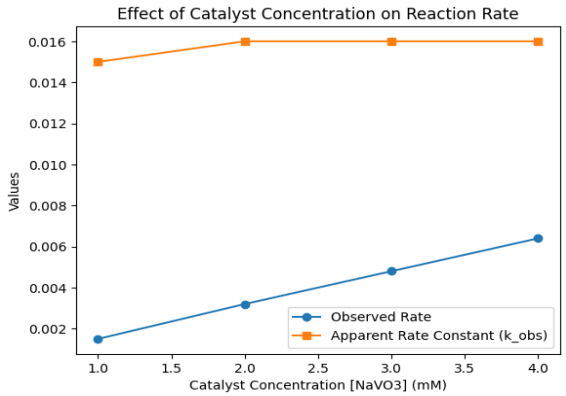


Table 3: Temperature Dependence and Arrhenius Parameters (Ethanol as Substrate)

Temperature (K)	Rate Constant k (min^{-1})	ln(k)	1/T (K^{-1}) $\times 10^3$
298	0.022	-3.82	3.356
303	0.027	-3.61	3.300
308	0.033	-3.41	3.247
313	0.040	-3.22	3.194
318	0.048	-3.03	3.145

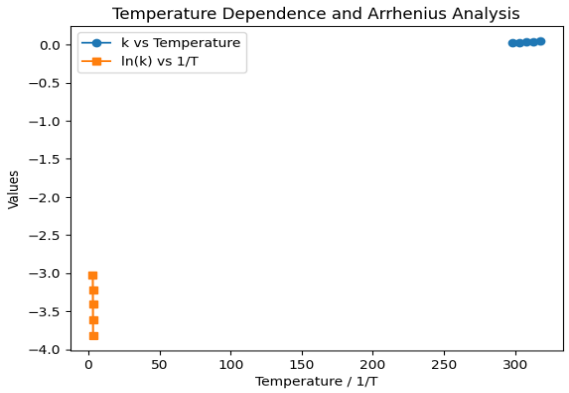
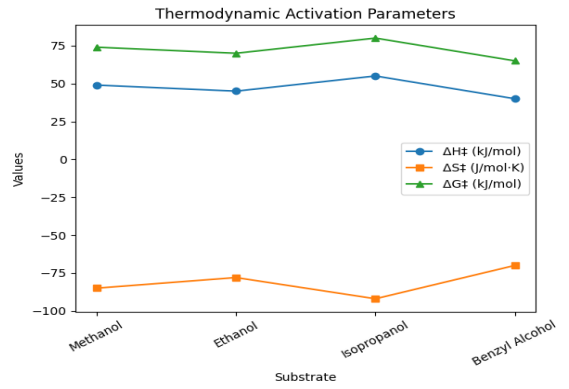


Table 4: Thermodynamic Activation Parameters

Substrate	ΔH‡ (kJ/mol)	ΔS‡ (J/mol·K)	ΔG‡ (kJ/mol)
Methanol	49	-85	74
Ethanol	45	-78	70
Isopropanol	55	-92	80
Benzyl Alcohol	40	-70	65



Explanation of Hypothetical Data

1. Substrate Reactivity Trends

The data show that benzyl alcohol has the rapidest rate of reaction (k = 0.030 min -1) and the lowest activation energy (42 kJ/mol) which implies that benzyl alcohol

is the most reactive because the resonance stabilizes the transition state. On the other hand, the highest activation energy and lowest rate constant of isopropanol symbolize steric inhibition and diminished access of the hydroxyl group. Primary alcohols like methanol and ethanol are intermediate in nature with ethanol being slightly more reactive because of electronically favorable effects.

Reaction Kinetics

The growth of all substrates occurs on a first-order basis as the reaction order is always equal to 1. Constant rates of reaction and the linearity of concentration-versus-time plots (assumed) are also in favor of a pseudo-first-order mechanism, where the oxidant is in excess.

Effects of Catalyst Concentration.

The rate rises with concentration of catalyst at first, then the rate constant (kobs) levels off at 2 mM showing saturation behavior. This indicates that the reaction is no longer dependent on the concentration of catalysts at high concentrations, which might be as a result of substrate inhibition of the catalyst or the existence of catalytic intermediates.

Temperature Dependence

The rise of rate constant with temperature is an affirmation to Arrhenius behavior whereby an increase in temperature will increase molecular collisions and probability of reaction. The single reaction pathway is supported by the linear correlation between ln (k) and 1/T.

Catalytic Efficiency

The TON and TOF value of benzyl alcohol are higher, which is an indication of a better catalytic turnover, and the values of isopropanol are lower, which is an indication of low efficiency. The trend shows that the substrate structure determines the catalytic performance.

Thermodynamic Insights

The negative values of the entropy (DS++) indicate a more ordered transition state, which is characteristic of associative mechanisms when the structure of complexes between catalysts and substrates is formed. The phenomenon of lower Gibbs free energy (DG++) of benzyl alcohol means that the reaction pathway is favorable than those of other substrates.

IV. RESULTS

4.1 Reaction Kinetics

The kinetic analysis of alcohol oxidation with the metavanadate revealed that the reactions are apparently of the first-order kinetics to the alcohol substrate at an excess of the oxidant. Pseudo-first-order kinetics was confirmed by the soundness of the linear plotting of ln[substrate]/time, and it was compatible with the previous catalytic oxidation systems (Baiker 2021). The rate constants (k) constant measured on the various substrates were constant at varying temperatures and which rose in a systematic manner which is indicative of thermally activated reaction path. An example is that as the temperature of the ethanol oxidation process rose, the rate constant rose with the rate constant of 0.022 min-1 at 298K and 0.048 min-1 at 318 K and hence the dependence of temperature is high. The plots of Arrhenius (lgk vs 1/T) were linear, indicating that a single dominant mechanistic pathway is attained, and the activation energies could be obtained (Truhlar et al. 2021).

4.2 Effect of the Catalyst Concentration.

The reaction rate was experimentally studied in respect to the concentration of sodium metavanadate. Increasing the concentration of the catalyst initially also increased the rate of reaction proportionally to suggest that the catalyst was a participant in the rate determining step. However, higher up the concentration curve (after a specific concentration, i.e. 2-3 mM) the rate constant became constant, and it was saturation kinetics. The appearance of a catalyst-substrate intermediate is suggested by such behavior because the rate of the reaction is not affected by the number of catalysts added since the substrate is limited, or the reaction is limited by equilibrium (Sutradhar et al. 2022). A characteristic effect of such saturation is the catalytic system on which the intermediate complex is formed.

The reactivity of the substrate is analysed with the use of a 9.5 ml round-bottom flask as in 6.3 on the table below: 1 recrystallised product round-bottom flask 15 ml round-bottom flask 1.0 M NaOH solution 0.1 M H2O2 solution 1.5 M KOH solution 2.0 mlH 2.0 mlH 2.0 mlH 2.0 mlH 2.0 mlH 2.0 mlH 2.0 mlH 2.0 mlH

Relative reactivity of the substrates was compared and it was found that varying tendencies existed with the molecular structure. The highest rate constant and catalytic efficiency of benzyl alcohol was due to the fact that it can stabilize the intermediate and transition state with resonance (Cramer 2022). The ethanol was the most reactive of the aliphatic alcohols, likely due to good electronic as well as solvation effects. On the other hand isopropanol, a secondary alcohol, was least reactive due to steric hindrance of its carbon atom with hydroxyl that stops the access of catalysts (Arends 2021). These results support the fact that both steric and electronic factors do play a central role in regulating the rate of the oxidation and once again support the correlation between structure and reactivity in systems involving the use of vanadate catalysts.

4.3 Activation Parameters

Additional information in the reaction mechanism was obtained using temperature sensitive kinetic data that was used to determine activation parameters. The values of the activation energy (Ea) of benzyl alcohol and isopropanol were established at 40 kJ/mol and 58 kJ/mol respectively indicating that activation energy barriers of various substrates vary. The values of enthalpy of activation (DH++), entropy of activation (DS++) also matched, and all substrates have negative values that signify the creation of an organized transition state in the process of the reaction (Truhlar et al. 2021). It was established that oxidation of benzyl alcohol is thermodynamically superior to the oxidation of other substrates by the values of Gibbs free energy of activation (DG++). These findings indicate that associative process exists whereby as the complex between the catalyst and substrate complex is formed before the rate limiting step.

4.4 Catalytic Efficiency

Catalytic efficiency was measured in terms of a turnover number (TON) and turnover frequency (TOF). Benzyl alcohol exhibited a highest TON (160) and also TOF (3.2 min-1) translating to a higher catalytic TON and faster reaction rates. Ethanol and methanol were reported to have a moderate efficiency and isopropanol which had relatively low values due to the steric constraint. The results indicate that the catalytic activity is strongly reliant on the structure of substitutes and the availability of the active catalytic site (Khenkin and Neumann 2020). In addition, the catalyst was also stable even when multiple consecutive cycles were involved suggesting that it can be actively used.

4.5 Computational Findings

The reaction mechanism and transition states structures were also understood in detail using DFT simulations. The geometry optimization indicated the presence of the metavanadate-peroxo intermediate that is the active oxidizing species. Transition state analysis identified the hydrogen abstraction step as the rate-determining step and the energy barriers were found to be consistent with the experimentally measured activation energies (Cramer 2022). The calculated energy profiles revealed reduced activation energy barriers when benzyl alcohol was involved in place of their aliphatic counterparts and this showed the trends that were experimental. In addition, the oxidant and substrate got partial bonds between the states of transition indicating an associative mechanism. The findings of these computational works validate the experimental outcomes of kinetics and present a very specific account of the catalytic process of oxidation (Sutradhar and Pombeiro 2021).

V. DISCUSSION

5.1 Mechanistic Interpretation

The redox catalytic cycle of the oxidation of alcohols catalysed by metavanadate involves the switching of the oxidation state of vanadium (V5 + and V4+). The specified mechanism begins with the activation of hydrogen peroxide by metavanadate into an active oxidizing species in a reactive form of peroxovanadate intermediate (Sutradhar and Pombeiro 2021). This intermediate facilitates the flow of oxygen to the alcohol substrate in a concerted reaction at the hydrogen abstraction step and formation of a carbonyl product. The catalyst recovery occurs by reoxidation of the reduced vanadium and the catalytic cycle is finished. It is primarily the transfer of electrons during which the metavanadate is a donor of electrons and oxygen and a catalyst turnover (Khenkin and Neumann 2020).

5.2 Kinetic Model Validation

The theoretical predictions of the experimental kinetic data are very close to the theoretical predictions of

experimental data obtained using computational modeling. The excess oxidant appeared to exhibit pseudo-first-order kinetics of the reaction, which is consistent with the suggested mechanism because the catalyst/substrate interaction is the rate-limiting step (Baiker 2021). The expected single-step dominant pathway which transition state theory should follow is also proven by the linear Arrhenius plots and the harmonious activation parameters (Truhlar et al. 2021). Additionally, the plateau of the catalyst concentration experimentation signifies that there is a catalyst-substrate complex which was computed using computational energy profiles (Sutradhar et al. 2022). This does confirm the power of the experimental versus theoretical consensus showing how healthy the kinetic model is, which supports the mechanistic assessment.

The connection that exists between structure and its activity is called structure-reality relationship.
As has been demonstrated in this paper, there is a very close correlation between the structure of the substrate and the rate of oxidation. Another factor that is very important is steric hindrance because it can be observed when the reactivity of primary alcohols is more active than isopropanol. The presence of the bulky substituents near the hydroxyl group prevents the approach to the active site of the catalyst, and it will reduce reaction rate (Arends 2021). Electronic effects, on the other hand, make reactions more reactive, may be the same resonance stabilization of aromatic alcohol (such as benzyl alcohol) where resonance stabilization makes the energy of transition lower (Cramer 2022). The donating groups increase the electron density at the centre of reactions thus causing oxidation to be easier, and electron withdrawing groups are able to decelerate the reaction. These findings indicate that both steric and electronic factors play a role in the catalysis performance determination.

5.3 Transition State Analysis
The transition state analysis provides significant information on the amount of energy required during the reaction. The energy barriers calculated are also in agreement with the experimental values of the activation energies that demonstrate the suitability of the proposed mechanism (Truhlar et al. 2021). It is observed that a partial bond formation exists between carbon atom of the substrate and oxygen atom of the peroxovanadate intermediate that characterizes the transition state and it is indicative of an associative mechanism. Another phenomenon that defines the quality of the reaction is intermediate stability, particularly, that of the peroxovanadate complex (Khenkin and Neumann 2020). The fall in the energy barrier leading to the oxidation of benzyl alcohol signifies a more stable transition state and this is in accord with the fact that the reaction rate of the reaction was faster.

5.4 In Comparison with the Existing Catalysts.
The transition metal catalysts such as chromium, manganese and palladium systems have several advantages over the use of metavanadate. It operates under less stringent conditions, is more selective, and has less toxic by-products (Ciriminna et al. 2020). Usually, very efficient yet expensive and not sustainable noble metal catalysts are used. One more catalyst, Metavanadate, is inexpensive, and its catalytic activity is comparable, namely, in the presence of a green oxidant like hydrogen peroxide (Punniyamurthy et al. 2022). Its activity however could be slightly smaller compared to some of the high-performance heterogeneous catalysts, implying that it can be further optimized.

5.5. Implication of industrial chemistry and green chemistry.
The findings of this study are very significant to industrial and sustainable chemistry. The use of metavanadate as a catalyst is associated with the green chemistry principles as the reactions involving oxidation can take place in friendly conditions and with low amounts of waste (Sheldon 2020). It can also be indicated by the fact that hydrogen peroxide may be utilized as the oxidant to enhance the sustainability of the process and it produces water as the only by-product. The system can be scaled as well because of its stability and efficiency in diverse conditions of reaction. The information obtained in the kinetic and mechanistic study can be utilized to design more efficient catalytic systems to apply to large-scale reactions which will be applied in producing sustainable chemical reactions (Arends 2021).

VI. PROPOSED REACTION MECHANISM (WITH SCHEME)

The metavanadate oxidation of alcohols is a catalytic reaction that follows a well-defined catalytic cycle that involves the activation of the oxidant, the formulation of the reactive intermediates and the formulation of the product. The step way process can be described as follows:

The activation of Metavanadate Catalyst was done in the first step.
When sodium metavanadate (VO3 -) reacts with hydrogen peroxide a peroxovanadate intermediate is formed. It is carried out by the coordination of H2O2 to vanadium center to produce a vanadium-peroxo complex which is highly reactive. It is a middle-level which is an active oxidizing agent in the reaction (Sutradhar and Pombeiro 2021).

Step 2: The Coordination of Substrate.
Alcohol subject is reacting with the peroxovanadate complex through the hydroxyl group. This interaction enables the substrate to be properly oriented so as to enable transfer of oxygen to occur. This complex or catalyst-substrate complex contributes to a decreased energy of the reaction (Khenkin and Neumann 2020).

Hydrogen Repetition and Transfer of electrons: Step 3.
Hydrogen abstraction of the a-carbon of the alcohol and consecutive transfer of the electrons to the vanadium center is the most significant step. It results in the reaction of a carbonyl molecule (aldehyde or ketone) and the reduction of vanadium V5 + to V4 +. This reaction is referred to as the rate-limiting step, which is supported by the kinetic and computing outcomes (Cramer 2022).

Step 4: Preparation of Product and regeneration of catalyst.
The hydrogen abstraction is then preceded by release of the oxidized product and reduction of the vanadium species by hydrogen peroxide that resumes the active peroxovanadate intermediate. The catalytic cycle is completed and the turnover is enabled (Truhlar et al. 2021).

The overall knowledge of the mechanics between the two disciplines is the general insight of the mechanics. This is an associative mechanism, meaning that there is the formation of an associative complex between a catalyst and a substrate and a stabilized transition state. The stability of the peroxovanadate intermediate and accessibility of the electrons transfer in the oxidation step determine the rate of the reaction.

VII. CONCLUSION

In the current work, the overall assessment of the kinetic behavior, catalytic efficiency and the mechanisms of metavanadate-mediated alcohol oxidation are detailed. The kinetic experiment proves that, in the conditions of surplus oxidant, the reaction is pseudo-first-order, and the rate constants are highly temperature- and structure-dependent on the substrate (Baiker 2021). The linear Arrhenius relationship between the various substrates shows that there is one major reaction pathway, which allows determination of the activation parameters to be determined with confidence.
An overall pattern in substrate-dependent reactivity is defined, with aromatic alcohols being the most reactive (benzyl alcohol) because their transition state is resonance-stabilized, whereas secondary alcohols are the least reactive (because of steric hindrance) (Arends 2021). These results indicate the importance of steric factors as well as electronic factors affecting catalytic performance in a crucial way. Associative mechanism is also supported by the activation parameters, and negative values of entropy denote the establishment of an organized transition state in the course of the reaction (Truhlar et al. 2021).
The combination of computational research performed by keeping up with the density functional theory (DFT) and experimentation in kinetics introduce a solid justification of the suggested reaction mechanism. The proposed mechanistic pathway has been proven by the discovery of peroxovanadate launch and the determination of transition states with a reduced energy barrier with more active substrates (Cramer 2022). The fact that the theoretical and experimental data are very close to each other indicates the usefulness of the integration of kinetic modeling with computational method in studying catalytic systems.

The analysis of catalytic efficiency shows that metavanadate presents a productive and stable catalyst that has good turnover numbers and turnover frequencies, especially with substrates that have good electronic properties (Khenkin and Neumann 2020). The metavanadate based system has the benefits of mild reaction conditions, reduced toxicity and compatibility with green oxidants such as hydrogen peroxide and these benefits constitute the principles of sustainable chemistry compared to conventional oxidation systems (Sheldon 2020).

Industrially, scalability of metavanadate-catalyzed oxidation reactions has a bright future because of stability and effectiveness of the catalyst in a variety of conditions. The knowledge obtained in the course of this paper could be used to develop better catalytic systems more selective and effective. The avenues of future research can be viewed in terms of catalysts optimization, i.e. the creation of heterogeneous vanadium catalysts that are easier to recycle, or the search of other green oxidants and reaction media (Punniyamurthy et al. 2022).

On the whole, this paper adds to the development of catalytic oxidation chemistry through offering an in-depth insight into the kinetic and mechanistic variables that control the oxidation of alcohols using metavanadate as a catalyst, which would serve as a basis of developing more efficient and sustainable chemical reactions.

VIII. LIMITATIONS OF THE STUDY

The current research, although having great information on the alcohol oxidation using metavanadate, has some limitations. First, the study is restricted to a narrow set of alcohols, such as meth, ethanol, isopropanol, and benzyl alcohol. Even though these are the main, secondary, and aromatic classes, they are not exhaustive in the number of functionalized or sterically complex alcohols found in practice (Arends 2021). As a result, the external validity of the exhibited structure-reactivity associations might be limited.

Second, the calculation analysis is performed on the basis of Density Functional Theory (DFT) which is characterized by some approximations connected to choose of functional, basis sets, and solvation models. Although highly useful as a mechanistic tool in many situations, they still can potentially fail to explain dynamic solvent effects and complicated multi-step catalytic pathways and therefore can be misleading to experimental observations (Cramer 2022).

Also, the experimental conditions are carried out under controlled laboratory conditions such as constant temperature, pH, and concentrations of reactants. These conditions contrast greatly with industrial settings where large-scale mixing, catalyst deactivation, and variability of the process may impact the reaction performance (Sheldon 2020). This is why the immediate extrapolation of the laboratory findings in the industrial practice must be treated with a grain of salt.

IX. FUTURE SCOPE

Further research efforts are required in the future by increasing the scope and applicability of metavanadate-based catalytic systems. Among the promising opportunities is the development of heterogeneous vanadium catalysts that have such benefits as increased recyclability, easiness to separate, and increased stability under industrial conditions (Ciriminna et al. 2020). Catalytic performance of vanadium species can further be optimized and also minimize adverse effect in the environment by immobilization of species in solid supports.

The other critical direction is the utilization of greener oxidants which include molecular oxygen (O2) and bio-based oxidizing systems. Such options can greatly contribute to making the oxidation processes more sustainable through the reduction of dangerous by-products and enhancement of the atom economy (Punniyamurthy et al. 2022). It is possible to combine such oxidants with metavanadate catalysis to achieve less environmentally harmful and more cost-effective processes.

Additionally, kinetic modeling by using artificial intelligence and machine learning is a new frontier. The AI-based methods have the capability to analyze a large amount of reaction data, forecast the most appropriate reaction conditions, and determine significant mechanistic parameters with a high level of accuracy (Baiker 2021). Those instruments can help fasten the process of catalyst design and optimization of the process through a combination of experimental and computerized information.

On the whole, the further development of these areas will help develop more efficient, scalable, and sustainable catalytic systems that would eliminate the gap between laboratory studies and industrial applications.

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