

# Kinetic Studies of Alcohol Oxidation Reaction by UV-VIS Spectroscopy

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## ABSTRACT

The selective oxidation of primary alcohols and secondary alcohols into their corresponding aldehydes (or carboxylic acids) and ketones is one of the most important transformations in modern organic synthesis. Tertiary alcohols resist oxidation by conventional oxidizing agents unless they are dehydrated in acidic media to alkenes, which subsequently undergo oxidation. Jones' reagent is a solution of chromium trioxide in dilute  $H_2SO_4$  which also affects the oxidation of primary allylic alcohols to aldehydes and secondary alcohols to ketones. Other chromium trioxide reagents have been prepared by adsorption of chromium trioxide on Celite, silica gel, or on anion exchangers. Among non-acidic reagents which are suitable for oxidations of acid-sensitive substrates, is Collin's reagent, a complex of chromium trioxide with two molecules of pyridine. It is prepared by the addition of chromium trioxide in small portions to pyridine, with continuous stirring and cooling the mixture in an ice bath. The disadvantages of this reagent are that a) it is very hygroscopic and is easily converted into the insoluble dipyridinium dichromate b) a six fold quantity of the reagent might be required to obtain best yields in some instances and c) saturated aliphatic alcohols often give low yields.

**KEY WORDS:** - Kinetic, Oxidation, UV-VIS spectroscopy, Chromate, Dowex-2, order of reaction

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## I. INTRODUCTION

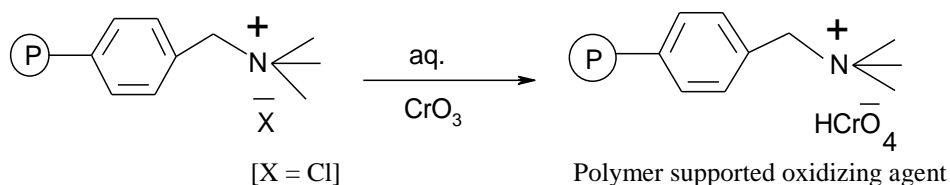
Transition metals in the higher oxidation state generally can be stabilized by chelating with suitable complex agent. The kinetics and mechanism of oxidation of chromates has been well studied. Reaction mechanism of various elementary reactions must be investigated to analyze the factors affecting the selectivity. In the present investigation, we report herewith the oxidation of 1-Phenylethanol by polymer- supported Chromate forms of Dowex-2 is used as an oxidant and find various activation parameters as well as order of reaction. Main reaction product acetophenone isolated and characterized. Thermodynamic parameters evaluated results under zero order conditions are in agreement with the rate law.

## II. EXPERIMENTAL

All commercially available materials were used as received, unless otherwise mentioned. Tetrahydrofuran was dried over anhydrous  $MgSO_4$  and distilled from sodium and benzophenone under  $N_2$ . Diethyl ether was refluxed with sodium and benzophenone and distilled immediately before use. Acetone and N,N-dimethylformamide were distilled with  $4\text{\AA}$  molecular sieves onto  $4\text{\AA}$  molecular sieves just before use.

### Preparation of supported oxidizing agent [1-3]

The supported oxidizing agent was prepared by reported method. The Chromate forms of Dowex-2 containing a quaternary ammonium group [ $10 \times 10^{-3} \text{ kg}$ ] was stirred with a saturated solution of periodates [ $5 \times 10^{-3} \text{ dm}^3$ ] in water [ $30 \times 10^{-3} \text{ dm}^3$ ] for 30 min at room temperature using a magnetic stirrer. The Chromate ion was readily displaced and Chromate form of resin was obtained in 60 min. The resin was successively rinsed with water, acetone and THF and finally dried in vacuum at 323 K for 7h. The dried form of the resin was stored and used throughout the kinetic study.



#### **Determination of the capacity of chromate form of the polymeric reagent [4]**

The capacity of Chromate form of Dowex-2 polymeric reagents was determined by iodometrically. The capacity of the chromate form of resin were 2.11 and 2.06 eq/L and used for kinetic study throughout work. The loading was also determined by elemental nitrogen analysis and were found to be 1.45 and 1.79 eq/L.

#### **Chemicals and Reagents**

All reagents used were of Analytical Grade and all solutions were prepared with double distilled water.

#### **Method of kinetics [5-7]**

The reaction mixture for the kinetic run was prepared by mixing alcohol, oxidant and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature  $318 \pm 1$  K. At different time interval, the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stoppered test tube containing  $5 \times 10^{-3}$  dm<sup>3</sup> of 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using SL 159 UV-visible spectrophotometer. Duplicate kinetic runs showed that the rate constants were reproducible to within  $\pm 1$  %.

### **III. PRODUCT ANALYSIS [8-10]**

The oxidation of 1-Phenylethanol leads to the formation of acetophenone. The product formed was analyzed by their 2, 4-dinitrophenylhydrazine derivatives. The yield of DNP recrystallisation with the DNP of acetophenone was 94%. The product also identified either by comparison with authentic samples or by UV, FT-IR spectral and elemental analysis.

IR spectra of all compounds were recorded as films cast on a salt plate from solutions in CH<sub>2</sub>Cl<sub>2</sub>. A Thermo Nicolet IR100 spectrometer with a resolution of 4 cm<sup>-1</sup> was used for this purpose. NMR spectra were obtained from IISER Kolkata, on a Joel Make ECS 400 NMR instrument. All spectra were obtained using CDCl<sub>3</sub> as the NMR solvent with residual CHCl<sub>3</sub> as the internal reference. Mass spectra were done on a Finnegan AQA Mass Spectrometer by the electro spray ionization (ESI) method. The yield was 0.09 g (96.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 6.91, 7.21 (d, J= 7.8 Hz, Ar H, 4H), 6-6.2 (m, -CH=, 1H), 5.3, 5.5 (dd, J= 18.1, 1.9, 11.4, 1.3 Hz =CH<sub>2</sub>, 2H), 4.61 (s, -CH<sub>2</sub>-, 2H), 4.51 (d, J = 5.5 Hz, -CH<sub>2</sub>-, 2H).

### **IV. RESULTS AND DISCUSSION [11-14]**

Functional groups such as ketones, aldehydes, carboxylic acids, esters, lactones, acid halides, anhydrides, amides and lactams show a strong C=O stretching absorption band in the region of 1870 to 1540 cm<sup>-1</sup>. The C=O stretching mode is always intense owing to the large dipole moment of the carbon-oxygen double bond. The absorption frequency occurring at approximately 1715 cm<sup>-1</sup> for a saturated aliphatic ketone is often referred to as the "normal" absorption frequency. Changes in the environment of the carbonyl group affect an increase or a decrease in the absorption frequency from this "normal" value. Conversely, changes in the observed absorption frequency can be interpreted as reflecting changes in the environment of the carbonyl group.

#### **Factors affecting frequency of absorption of the C=O group**

The position of the C=O stretching band is determined by a number of factors including: (1) the physical state, (2) electronic and mass effects of neighboring substituent's, (3) conjugation, (4) hydrogen bonding (intermolecular and intramolecular) and (5) ring strain. Intermolecular hydrogen bonding between the carbonyl group and a hydroxylic solvent causes a slight decrease in the absorption frequency. The physical state of the carbonyl compound, ex. the crystal packing structure can affect a slight increase in the absorption frequency

#### **Effect of varying weights of oxidant**

The order with respect to weights oxidant is zero, as the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant between 20 to 40 x 10<sup>-6</sup> kg of oxidant at constant concentration of solvent (1, 4- dioxane, 5 x 10<sup>-3</sup> dm<sup>3</sup>) and 1-Phenylethanol (12.3 x 10<sup>-3</sup> mol/dm<sup>3</sup>), the effect of varying weights of oxidant on zero order rate constant as shown in Table-1.

**Table-1. Effect of varying weights of oxidant on reaction rate at 318 K.**

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Oxidant $\times 10^{-6} \text{ kg} \rightarrow$	20	25	30	40
Chromate form of Dowex-2	1.76	1.77	1.78	1.79

**Effect of varying concentrations of 1-Phenylethanol**

At a varying concentration of 1-Phenylethanol [ $7.80$  to  $15.8 \times 10^{-3} \text{ mol/dm}^3$ ], constant weights of oxidant [ $70 \times 10^{-6} \text{ kg}$ ] and constant concentration of solvent [1,4-dioxane,  $5 \times 10^{-3} \text{ dm}^3$ ], zero order rate constant [Table- 2] were found.

**Table-2 Effect of varying concentrations of 1- Phenylethanol**

Rate constant	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
1 –Phenyl ethanol	$7.80 \times 10^{-3} \text{ mol /dm}^3$	$9.25 \times 10^{-3} \text{ mol /dm}^3$	$10.4 \times 10^{-3} \text{ mol /dm}^3$	$15.8 \times 10^{-3} \text{ mol /dm}^3$
Chromate form of Dowex-2	1.35	1.37	1.38	1.39

**Effect of varying dielectric permittivity of the medium on the reaction rate**

It was found that as the dielectric constant of the medium increased, this including  $r^* < r$  [Where  $r^*$  and  $r$  refer to the radii of the reactant species and activated complex respectively] at constant concentration of 1-Phenylethanol [ $7.80 \times 10^{-3} \text{ mol/dm}^3$ ] and constant concentration of oxidant [ $70 \times 10^{-6} \text{ Kg}$ ], solvent [ $5 \times 10^{-3} \text{ dm}^3$ ] as shown in Table-3.

**Table-3. Effect of varying dielectric permittivity**

Rate constant	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Solvent [ $5 \times 10^{-3} \text{ dm}^3$ ]	$\text{C}_6\text{H}_{12}$	$\text{CCl}_4$	1,4-dioxane	$\text{CHCl}_3$
Dielectric constant	2.10	2.17	2.30	3.25
Chromate form of Dowex-2	1.19	1.30	2.32	2.48

**Effect of varying temperature**

It was observed that, the rate of reaction increased with an increase in the temperature. [Table-4]. The activation parameters like energy of activation [Ea], enthalpy of activation [ $\Delta H^\ddagger$ ], entropy of activation [ $\Delta S^\ddagger$ ] free energy of activation [ $\Delta G^\ddagger$ ] the high positive values of free energy of activation indicates that the transition state is highly solvated and frequency factor [A] were calculated by determining values of k at different temperatures. [Table-5].

**Table - 4. Effect of varying temperature**

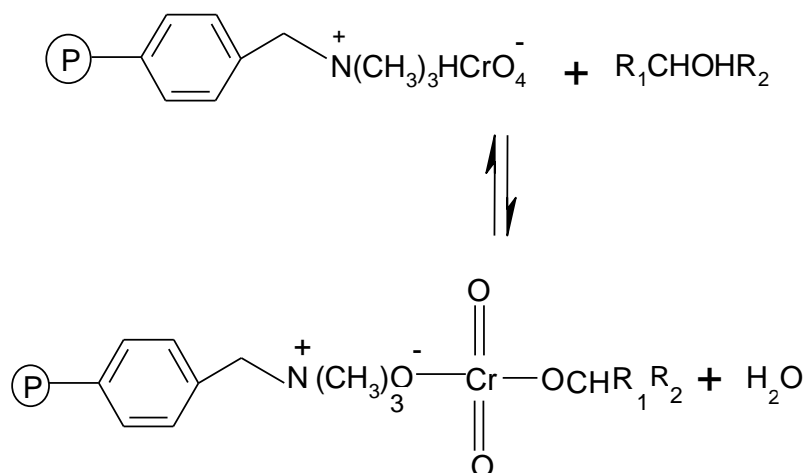
Rate constant	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Temperature K	313	318	323	328
Chromate form of Dowex-2	1.54	1.85	2.14	2.35

**Table -5. Activation parameters**

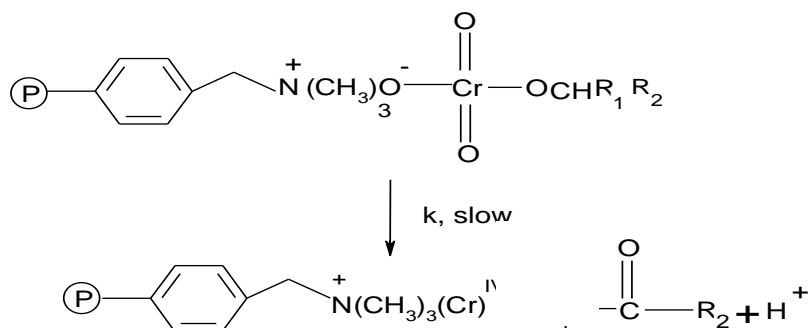
[Ea] KJ mol <sup>-1</sup>	[ $\Delta H^\ddagger$ ] KJ mol <sup>-1</sup>	[ $\Delta S^\ddagger$ ] JK mol <sup>-1</sup>	[ $\Delta G^\ddagger$ ] KJ mol <sup>-1</sup>	[A] X 10 <sup>-5</sup> s <sup>-1</sup>
$75 \pm 4$	$57 \pm 3$	$-75 \pm 2$	$310 \pm 2$	$34 \pm 0.5$

The mechanism is suggested in Scheme I and involves ester formation.

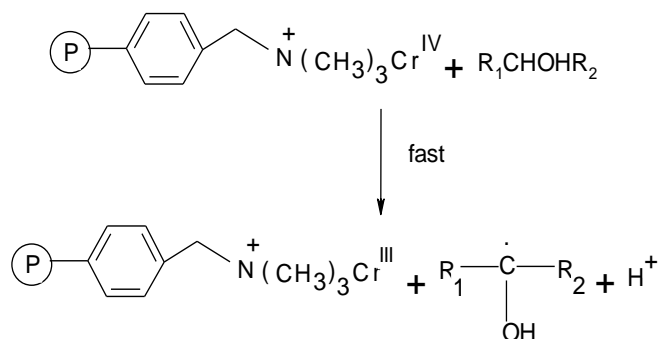
1) The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester.



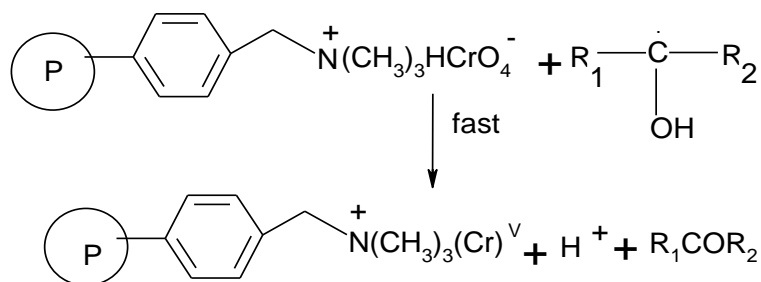
2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.



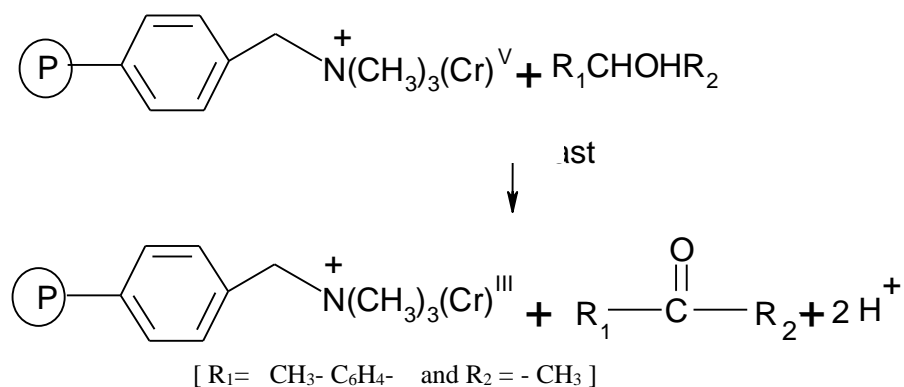
3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture.



4) Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium (V).



5) The intermediate chromium (V) in the last step reacts with 1-Phenylethanol produce acetophenone.



**Scheme I**

## V. CONCLUSION

The oxidation of alcohols to their corresponding carbonyl compounds was carried out by the TEMPO-TCCA oxidation system as well as by the PEG-supported TEMPO. The reactions proceeded to completion without over-oxidation to the corresponding carboxylic acid in most cases. Polymer supported catalysts are being currently regarded as amenable alternatives to improve the efficiency of a catalytic process in that they allow catalyst recovery and recycling. Removal of the catalyst can be achieved by mere precipitation, making the purification of the product much easier. Both methods provide mild conditions for oxidation of alcohols, and are viable alternatives to metal based oxidants. The IR spectra of the carbonyl compounds obtained have been studied, and trends in absorption frequencies of the carbonyl group have been discussed. We obtained zero order dependence [15-16] with rate constant  $k$  of the second slow step in which product acetophenone was obtained. Based on the experimental observations a probable mechanism is suggested.

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