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"UV- Vis Spectroscopic Study of Oxidation of Phenol by Quinalidinum Cholorochromate in Aqueous Acetic Acid Medium"

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Abstract

The oxidation of phenol by Quinalidinum Cholorochromate (QuCC) has been studied spectrophotometrically at 316.4 nm in aqueous acetic acid medium. The kinetics of oxidation of phenol and effect of various factors on the rate of oxidation reaction was also studied. The reaction was found to be first order with respect to concentration of QuCC, phenol and with respect to acid concentration [H^+]. The effect of ionic strength, solvent polarity was also studied on rate of reaction and the rate of oxidation reaction found to be increases with increase in ionic strength and at low dielectric constant of the medium. The main oxidation product of phenol has been identified as corresponding 1-4 benzoquinone.

Key words: UV-Vis Study, Kinetics, Oxidation, Phenol, Quinalidinum Cholorochromate, Solvent Polarity, Dielectric Constant.

Introduction

The oxidation of phenol to quinone is a fundamental chemical transformation with significant implications across organic synthesis, biological systems, and industrial applications. Quinones, particularly para-benzoquinone, serve as key intermediates in the production of dyes, pharmaceuticals, and agrochemicals, and play crucial roles in redox biology and enzymatic processes The kinetics of oxidation of phenols were studied by different chromium containing reagents such as isoquinolinium bromochromate[1], oxochromium(IV)ion[2], pyridinium fluorochromate[3], Benzyltrimethylammonium Chlorobromate.[4]

The kinetics and mechanism of oxidation of Cr (VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with efficient and stable reagent which is able to work as

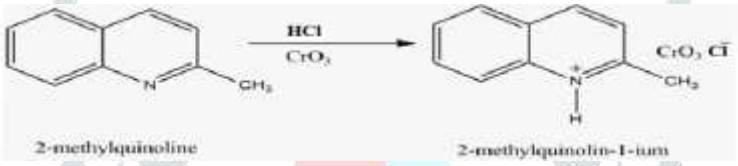
both a diverse substrate. The development of newer chromium (VI) reagents for the oxidation of organic substance will continue to be of interest.

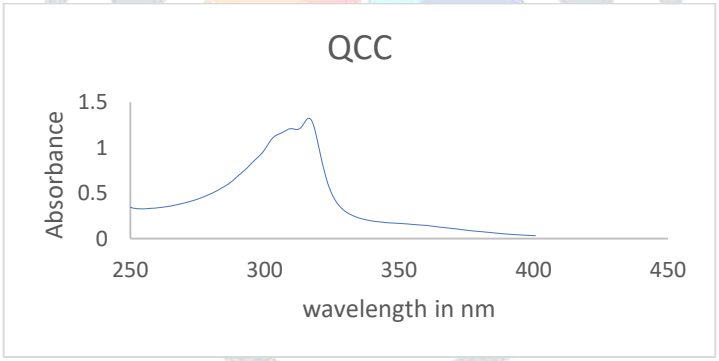
Experimental

All the chemicals used were od SD fine and are of laboratory grade and purified by recrystallisation or distillation and used for kinetics study. All other chemicals used were of LR grade was used. Substrate solutions were prepared in acetic acid. The absorption measurements were made with UV-Vis spectrophotometer of make Shimadzu 1800.

Preparation Of Quinalidinum Chlorochromate

Chromium trioxide (10 g, 0.1 mol) was dissolved in water (25 ml) and cooled to 0^0C. To this solution hydrochloric acid (6M,12 ml) was added drop wise during 10 min. To this resulting solution 2-methylquinoline or quinaldine (14 g, 0.1 mol) was added and then cooled for 2hr and filtered. The resulting mustered yellow crystal were dried and recrystallized. The purity of sample checked by iodometric method. The reagent melting point is 108-110^0C and molecular formula [$C_{10}H_8NHCrO_3$-Cl]





UV Spectrum of Quinalidinum Chlorochromate

The UV spectrum of quinalidinum chlorochromate was recorded on UV spectrophotometer of make Shimadzu-1800 and sample was scanned from 250 nm wavelength to 390 nm wavelength. The maximum absorbance is shown at wavelength 316.4 nm.

General Procedure for Oxidation of Phenol

Oxidation reaction of phenol was performed under sulphuric acid catalyzed conditions. Maintaining an excess concentration of QuCC, over the phenol solution, the two solutions were prepared in a 50% acetic acid-water mixture. The reaction mixture was stirred for 4 hours to ensure that the reaction reached completion. Next, the

reaction mixture was evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was maintained in a water bath to evapo-rate the ether followed by cooling in an ice bath to yield the product (M.P.115^{0}C). The product was dissolved in benzene, and a careful TLC analysis was performed with phenol as references. Only one spot corresponding to 1-4 benzoquinone was observed. The formation of 1-4 benzoquinone was further confirmed by recording and comparing M.P. with known sample.

Product Of Oxidation Of Phenols By QuBC

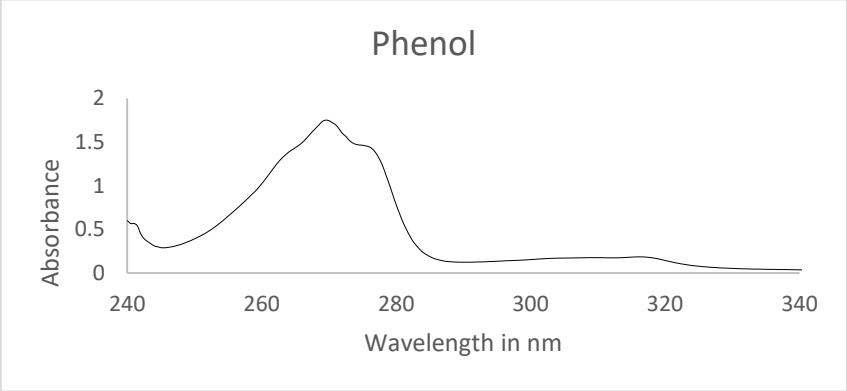
Phenols	Product	MP ^{0}C Reported
Phenol	1-4 benzoquinone	115

UV spectroscopic study of oxidation of phenol

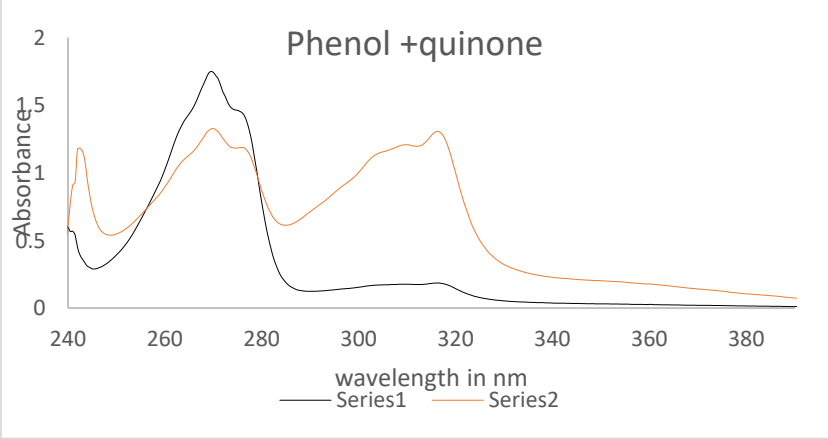
The UV spectrum of phenol and mixture of phenol and QuCC was recorded on UV spectrophotometer of make Shimadzu-1800 and kinetics measurement done with visible spectrophotometer of make Systronic 106.

UV spectrum of Phenol

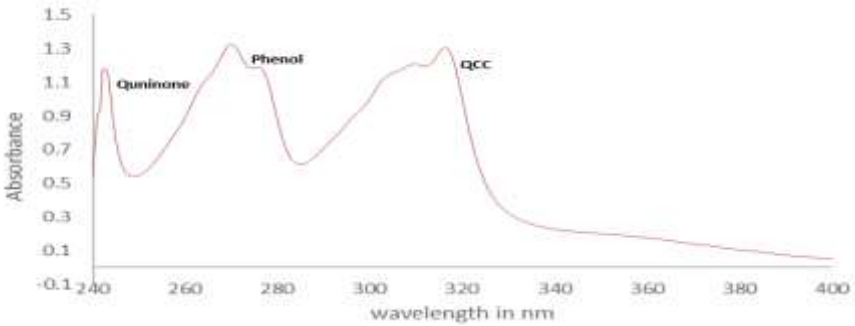
The UV Vis spectrum was recorded on UV Vis spectrophotometer which shows absorbance at 270 which is in accordance with previously recorded UV spectrum of phenol reported by Liu.[5]



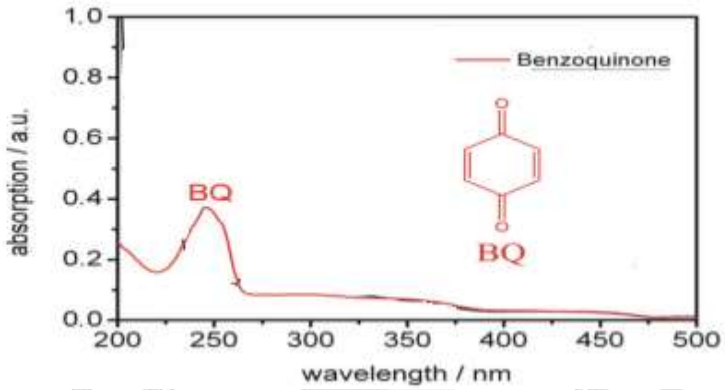
Recorded UV Spectrum of Phenol



UV spectrum of Quinone +Phenol and Unreacted QCC



UV spectrum of Quinone +Phenol and Unreacted QCC



[UV-Vis spectra of 1,4-benzoquinone (red) shows strong absorption with a maximum at 244 nm, (Open Journal of Physical Chemistry . Vol.3 No.2, May 2013) Thorsten Wilke, Michael Schneider, Karl Kleinermanns]

Result And Discussion

The study of oxidation of phenol was monitored by UV Vis Spectrophotometer. For the study equal quantity of each phenol, QuCC solution of same concentration were prepared in 50% of acetic acid solution then 2M sulphuric acid was mixed with solutions in with in beaker. Immediate after mixing the the solution the UV-Vis spectrum was recorded at wavelength 316 nm. It was observed that the absorbance value of phenol (270 nm) decreases as time passes with time indicating the decreasing peak height of phenol. The new absorbance peak is developed at 244 nm indicating that the phenol was getting converted in to 1-4 benzoquinone whose value is recorded by Thorsten Wilke et al.[6**],** the absorbance peak near (316 nm) shows that still reaction was incomplete there is still unreacted QuCC..

Kinetics Measurment

The reactions were stuided in pseud order conditions by taking concentration of phenol at least ten times greater than the concentration of reagent. The reaction completion was monitored up to 80% of completion on UV Vis spectrophotometer.

Phenol (10ml) and QuCC (10ml) of fixed concentration in 50% acetic acid as solvent were taken in two separate test tubes. The reactant was then mixed with proper shaking and required quantity of sulphuric acid were added in mixture and immediately stop watch was started. The course of reaction was followed by measuring the absorbance of reaction mixture at different time interval. The rate constant of reaction was calculated by measuring the slope of the graphs plotted in between Log (Abs) Vs Time.

Result And Discussion

A] Effect of Variation of Substrate Concentration

At constant concentrations of QuCC and H_2SO_4, the increase in amount of substrate enhances the reaction rate (Table 1). The plot of log k vs. log [substrate] for different initial concentrations of substrate found to be linear with unit slope, indicating the first order dependence of reaction rate on substrate.

Dependence of Rate Constant on [substrate]. Conditions: [QuCC] = 0.001 M,[H_2SO_4] = 1 M, Temp. = 303 K, Solvent = 50% Acetic Acid (V/V)

Substrate(M)	Phenol
0.12	14.83
0.08	10.64
0.06	7.48
0.04	5.39
0.02	2.62

B] Effect Of Variation Of QuCC Concentration

At constant concentrations of substrate and H_2SO_4 the increase in concentration of QuCC did not affect the rate of reaction. The first order plots of log [QuCC] vs. time found to be linear. The pseudo first order rate constants computed from the plots remained unaffected by the change in [QUCC], establishing the first order dependence of the reaction rate on QuCC in all cases.

Dependence of Rate Constant on [QuCC]. Conditions: [Substrate] = 0.001 M, [H_2SO_4] = 2 M, Temp. = 303 K, Solvent = 50% Acetic Acid (V/V)

Substrate(M)	Phenol
0.001	5.59
0.002	5.48
0.004	5.42
0.006	5.46

C] Effect of Ionic Strength

The change in concentration of KCl affects the rate of oxidations. The rate of reaction decreases with increase in concentration of KCl, most possibly due to the formation of less reactive species by interaction between Cl^- ion and protonated QuCC. [7]

Dependence of Rate Constant on [KCl]. Conditions: [Substrate] = 0.04 M,[H_2SO_4] = 2 M, [QuCC]=0.001 M Temp. = 303 K, Solvent = 50% Acetic Acid (V/V)

KCl (M)	Phenol
0.02	2.62
0.01	1.89
0.005	1.26
0	0.39

D] Effect of Solvent Composition

At fixed ionic strength and [H^+], the rate of oxidation of phenols with quinalidinum chlorochromate increases with decrease in polarity (or dielectric constant) of solvent. This is due to polar character of transition state as compared to the reactant The plot of log k vs. 1/D (dielectric constant) is linear with positive slope indicating ion-dipole type of reaction.[7]

Dependence of Rate Constant on Solvent Composition.

Conditions: [Substrate] = 0.04 M, [H_2SO_4] =2 M, [QuCC] = 0.001 M, Temp. = 303 K, Solvent = 50% Acetic Acid (V/V)

% Acetic acid and Water	1/D	Rate
30	0.01798	4.11×10^{-3} s^{-1}
40	0.02238	4.78×10^{-3} s^{-1}
50	0.02604	5.59×10^{-3} s^{-1}
60	0.03170	6.19×10^{-3} s^{-1}

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