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Mechanism Of Picolinic Acid Catalysed Quinaldinium Chlorochromate Oxidation Of Phenol

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Abstract: The kinetics of picolinic acid (PA) catalyzed quinaldinium chlrochromate oxidation of phenol is studied in 60% acetic acid – water (v/v) medium. The reaction shows unit order dependence each with respect to oxidant, picolinic acid and substrate. The reaction is acid catalyzed and the medium of low dielectric constant favours for the reaction. Increase in ionic strength has no effect on the reaction rate. The reaction does not induce the polymerization of acrylonitrile. The reactions are carried out at four different temperatures and activation parameters have been calculated. A suitable mechanism consistent with the observed kinetics has been proposed.

Key words: Oxidation, Phenol, Quinaldinium Chlorochromate, Picolinic acid.

Introduction

Chromium compounds have been used in aqueous and non-aqueous media for oxidation of variety of organic compounds.¹⁻⁷ Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents capable for oxidizing almost all the oxidizable organic functional groups⁸⁻¹². Quinaldinium chlorochromate (QnCC) has advantages in terms of ease of preparation, lower acidity, reaction period and yield of products. It is very stable and can be stored for longer periods without much loss in activity and hence turns out to be a very useful reagent in synthetic organic chemistry¹³. The structure of QnCC is,



Quinaldinium Chlorochromate

Phenol is an organic compound with the chemical formula C_6H_5OH . It is a white crystalline solid at room temperature. The molecule consists of a phenyl group (- C_6H_5) bonded to a hydroxyl group (-OH). It is mildly acidic, but requires careful handling due to its propensity to cause burns. It is an important industrial

commodity as a precursor to many materials and useful compounds¹⁴. Its major uses involve its conversion to plastics or related materials. phenol and its chemical derivatives are key for building polycarbonates, epoxides, bakelite, nylon, detergents and a large collection of drugs and herbicides. Picolinic acid (PA) can form a relatively stable complex with chromium (VI). The complex Cr(VI) PA/Cr(V)PA is more reactive than the oxidant. It has been reported¹⁵⁻¹⁶ that the picolinic acid catalysis is highly specific and related to the proximity of the nitrogen atom and the carboxylic acid group. This investigation was undertaken to gain a clear understanding for the mechanism of the quinaldinium chlorochromate oxidation of phenol.

Experimental

Materials

Commercial sample of phenol (E.Merck) is collected and purified before used. All other chemicals used were of AnalaR Grade.

Quinaldinium Chlorochromate (QnCC)

Chromium trioxide (10 g) was dissolved in 18.4 ml of 6 M hydrochloric acid solution was cooled to 0 0 C and to this 13.9 ml of quinaldine was added drop wise during 30 minutes. The reaction mixture was cooled for 2 h. The resulting yellow colored solid was collected and washed with ether kept under suction until moderately dried and placed under vacuum pump to get a dry powder. (Melting point 139 0 C).

Acetic Acid

Glacial Acetic acid (AR) (2 litre) was partially frozen and about 1 litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30 g) for 4 h and fractionally distilled. The distilled portion was collected between 116-118 $^{\circ}$ C, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractioned again after treating with chromium trioxide (30 g). The boiled fraction was collected 116-118 $^{\circ}$ C and kept in brown bottles.

Triply distilled water was used for the preparation of solutions.

Kinetic measurements

The reaction was carried out under pseudo- first order conditions by maintaining the substrate concentration in excess of quinaldinium chlorochromate. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the desired value and thermostated. The reaction was started by adding the oxidant to the mixture and aliquots were removed at definite time intervals and the decrease in concentration of quinaldinium chlorochromate by digital photoelectric colorimeter at 470 nm. The rate constants were obtained from the slope of the plot of log absorbance versus time by the least square method. The results were reproducible within ± 1 .

Product Analysis

To the substrate (0.1 M) in acetic acid, QnCC (0.1 M) was added and the medium was maintained acidic using perchloric acid. After slight warming the reaction mixture was maintained at room temperature for two days then the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ether layer was separated and then evaporated on a hot water bath to get the solid product. From the IR and GC-MS, it was confirmed that the product obtained was only *para*- benzoquinone¹⁷⁻¹⁸.

Results And Discussion

Effect of varying [QnCC]

The kinetic data reveals that the oxidation of phenol by quinaldinium chlorochromate is first order with respect to the oxidant. The plot of log absorbance versus time is linear indicating that the order with respect to QnCC is unity (Figure 1). The pseudo-first order rate constants were found to be independent of initial concentration of QnCC (Table 1).

Effect of varying [Phenol]

The reaction was carried out by varying the concentration of phenols keeping the other variables constant. The rate of reaction increased with increase in the concentration of phenol and the plot of $\log k_1$ versus

log [s] gave a straight line with a slope of unity (Figure 2) showing a first order dependence on the substrate. This was further well confirmed by the constancy of the specific reaction rate $k_2 = k_1 / [s]^{19}$ (Table 2).

Effect of varying [Picolinic acid]

The reactions were carried out with the varying concentrations of picolinic acid, while keeping the concentrations of other reagents constant. The rate of the reaction increases with increase in the concentration of picolinic acid (Table 3). The order with respect to picolinic acid was found to be one as evidenced by a plot of log k_1 *versus* log [PA] (Figure 3) which was linear with a slope of unity.

Effect of varying the hydrogen ion concentration

The reaction was followed with different concentration of hydrogen ions keeping the concentration of quinaldinium chlorochromate and substrate constant. The rate has been found to increase with increase in concentration of H⁺ (Table 4). A plot of log k₁ *versus* log [H⁺] give a straight line (Figure 4) with a slope of 1.34 (r = 0.999). Since the plot of log k₁ *versus* log [H⁺] did not give an ideal slope of unity. It is not possible to take the order with respect to [H⁺] as one and it can be concluded that the reaction is simply an acid catalyzed one²⁰.

Effect of varying solvent composition

The reaction rate was measured at different acetic acid-water mixtures. It was observed that an increase in the percentage of acetic acid considerably increased in the rate of the reaction (Table 5). The plot of log k_1 *versus* D^{-1} gave a straight line with a positive slope²¹ (Figure 5) suggests the involvement of an ion-dipole interaction in the rate determining step.²²



Figure 1. Plot of log absorbance versus time

Table -1 Dependence of rate con	nstant on oxidant concentration
$[Phenol] = 300 \times 10^{-2} mol dm^{-3}$	$A_{c}OH-H_{2}O = 60.40(\%)$

 $[H^+] = 2.00 \times 10^{-1} \, mol \, dm^{-3}$

AcOH-H₂O = 60:40(%)[PA] = $5.00 \times 10^{-4} mol \ dm^{-3}$ Temperature = $313 \ K$

[QnCC]×10 ³ mol dm ⁻³	$\frac{\mathbf{k}_{1}\times10^{4}}{s^{-I}}$
0.50	13.22
1.00	13.35
1.35	13.45
1.61	13.53
2.14	13.28



Figure 2. Plot of log k₁ versus log [substrate]

Table –	2 L)epend	lence	of rat	te cons	tant or	ı phenol	concent	ration
		-	2	2			-		

$[0, CC] = 1, 00, 10^{-3}$		
$[QnCC] = 1.00 \times 10^{\circ} mol$	dm° AcOH-H ₂ O = 60:40)(%)
$[\mathrm{H}^+] = 2.00 \times 10^{-1} mol dm$	$[PA] = 5.00 \times 10^{-4} mo$	ol dm ⁻³
	Temperature $= 313$	K
[Phenol]×10 ²	$k_1 \times 10^4$	
mol dm ⁻³	s ⁻¹	
1.50	6.00	
3.00	13.35	
4.50	19.95	
6.00	26.30	
7.50	38.02	





Table – 3 Dependence of rate constant on picolinic acid concentration

 $[QnCC] = 1.00 \times 10^{-3} mol \ dm^{-3}$ [Phenol] = 3.00 \times 10^{-2} mol \ dm^{-3} $[H^+] = 2.00 \times 10^{-1} mol dm^{-3}$ AcOH-H₂O = 60:40(%) Temperature=313 K

		Temperature=313
[PA]×10 ⁴	₩3 ₁ -3∰0 ⁴	
тд0dm -3	1 5 . ¹ 84	
2.50	68008	
30.6 0	289.46	



Figure 4. Plot of log k₁ versus log [H⁺]

Table – 4	Dependence	on rate	constant	on	acidity
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[QnCC]= $1.00 \times 10^{-3} mol dm^{-3}$ [Phenol]= $3.00 \times 10^{-2} mol dm^{-3}$

AcOH-H₂O = 60:40(%)[PA] = $5.00 \times 10^{-4} mol dm^{-3}$ Temperature = 313 K

	remperature = 5
$[{\rm H}^+] \times 10^1$	$k_1 \times 10^4 s^{-1}$
mol dm ⁻³	
1.05	3.69
1.58	6.91
2.00	13.35
3.00	17.38
3.98	21.87
4.23	31.62



Figure 5. Plot of log k₁ versus D⁻¹

		1
AcOH-H ₂ O (% v/v)	D	$k_1 \times 10^4$ s ⁻¹
50:50	43.08	11.67
55:45	39.99	12.18
60:40	35.69	13.35
70.30	28 31	15 51

Table - 5 Dependence on rate constant on solvent composition $[QnCC] = 1.00 \times 10^{-3} mol \ dm^{-3}$ $[H^+] = 2.00 \times 10^{-1} mol \ dm^{-3}$

Effect of varying the ionic strength

 $[Phenol] = 3.00 \times 10^{-2} mol \ dm^{-3}$

The reaction was studied with varying concentration of sodium perchlorate and keeping the other variables constant. The results indicate that ionic strength has negligible effect on the reaction rate, which confirmed the participation of an ion and neutral molecule in the rate determining $step^{23}$ (Table 6).

 $[PA] = 5.00 \times 10^{-4} mol dm^{-3}$ Temperature = 313 K

Effect of added acrylonitrile

The added acrylonitrile has no effect on the reaction mixture indicating the absence of free radical mechanism. No turbidity was obtained.

Effect of varying the manganous sulphate

The reaction was carried out with the varying concentrations of Mn^{2+} ions keeping all the other factors constant. The added Mn^{2+} ions have decreased the rate of the reaction. It indicates that two electron transfer process may be involved in the reaction (Table 7).

Table – 6 Dependence on rate constant on ionic strength

[NaClO ₄]	×10 ⁴	$k_1 \times 10^4$		
$[PA] = 5.00 \times 10^{-4}$	mol dm ⁻³		Temperature = 313	Κ
$AcOH-H_2O = 60:4$	40(%)		$[Phenol] = 3.00 \times 10$	$\int^2 mol \ dm^{-3}$
$[QnCC] = 1.00 \times 1$	10^{-3} mol dm	3	$[\mathrm{H}^+] = 2.00 \times 10^{-1} n$	ıol dm ⁻³

[NaCIO ₄]	×10	$\mathbf{K}_1 \times \mathbf{I} 0$
mol dm ⁻³		s ⁻¹
0.00		13.35
0.25		13.45
0.50		13.55
0.75		13.62
1.00		13.69

<i>Tuble 7 Dependence on fute constant on manganous surpliate concentrations</i>
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$[QnCC] = 1.00 \times 10^{-3} mol di$	m^{-3} [H ⁺] = 2.00×10 ⁻¹ mol dm ⁻³
$cOH-H_2O = 60:40$ (%)	[Phenol] = $1.00 \times 10^{-2} mol dm^{-2}$
$[PA] = 5.00 \times 10^{-4} mol dm^{-3}$	Temperature $= 313 \text{ K}$
$[MnSO_4] \times 10^4$	$\mathbf{k}_1 \times 10^4$
mol dm ⁻³	s ⁻¹
0.00	13.35
0.25	12.28
0.50	12.20
0.75	12.11
1.00	12.01

Effect of varying the temperature

The reaction has been studied at four different temperatures keeping all other factors constant. The thermodynamic parameters have been calculated (Table 8) from the least square procedure of a linear plot of ln (k_2/T) versus 1/T (Figure 6) using Eyring's equation.

 $H^{\#} = 19.89 \ kJmol^{-1}$ $S^{\#} = -208.23 \ JK^{-1}mol^{-1}$ $G^{\#} = 94.01 \ kJmol^{-1}$ at 313 K $Ea = 22.49 \ kJmol^{-1}$ at 313 K



Figure 6. Plot of ln k₂/T versus 1/T

Table – 8 Dependence on rate constant on temperature

 $[QnCC] = 1.00 \times 10^{-3} mol \ dm^{-3} \qquad [H^+] = 2.00 \times 10^{-1} mol \ dm^{-3}$ $[Phenol] = 3.00 \times 10^{-2} mol \ dm^{-3} \qquad [PA] = 5.00 \times 10^{-4} mol \ dm^{-3}$ $AcOH-H_2O = 60:40(\%)$

Temperature	$k_1 \times 10^4$
Κ	s ⁻¹
303	9.18
313	13.35
323	16.80
333	20.73

Mechanism and Rate law

From the experimental results, it is clear that the reaction is showing unit order with respect to oxidant, substrate and picolinic acid. The reaction is acid catalysed one.

Based on the above observations, a probable mechanism is given in scheme – I.







Rate law:

These above observations suggest that the rate law can be shown as,

rate = k [Phenol]
= Kk [Phenol] [HCrO₄⁻] [PA] [H⁺]²
[PA_T] = [PA] + [PA H⁺]
$$\therefore$$
 [PA] = $\frac{[PA_T] Ka}{Ka + [H^+]}$
rate = $\frac{KKa k [PA_T] [HCrO_4^-] [Phenol] [H^+]^2}{Ka + [H^+]}$
rate = k₃ [Phenol] [HCrO₄⁻] [PA_T]

Conclusion

The kinetics of picolinic acid catalyzed quinalidinium chlorochromate oxidation of phenol in aqueous acetic medium leads to the formation of complex and finally gives the product. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

References

- 1. Westheimer F.H., Chem Rev., 1949, 45, 419-423.
- 2. Waters W.A., Mechanism of Oxidation of Organic Compounds, Methuen, London 1964.
- 3. Stewart R, Oxidation Mechanisms, Applications to Organic Chemistry, Benjamin, New York 1965.
- 4. Sundaram S. and Venkatasubramanian N., Sci. Ind. Res., 1976, 35, 518-521.
- 5. Cainelli G. and Cardillo C., Chromium Oxidations in Organic Chemistry, Springer-Verlag, Berlin, Heidelberg, 1984, 5.
- 6. Hudlicky M., Oxidation in Organic Chemistry, American Chemical Society, Monograph, Washington, 1990, 186.
- 7. Muzart J., Chem. Rev., 1992, 92, 113-116.
- 8. Waters W.A., Quart. Rev., 1958, 12, 277-284.
- 9. Wiberg K.B., Oxidation by Chromic acid and Chromyl Compounds Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965, 69.
- 10. Lee D.G, in. Oxidation-Techniques and Applications in Organic Synthesis, ed. R.L.Augustine, Marcel Dekker, New York, 1969.
- 11. House H.O., Modern Synthetic Reactions, 2nd Ed., Benzamin, New York, 1972,459.
- 12. Rihter B. and Masnovi J., J. Chem. Soc. Chem. Commun., 1988, 35-42.
- 13. Degirmenbasi N. and Ozgun B., Monatshefte fur chemie., 2004, 135, 407-411.
- 14. Manfred Weber, Markus Weber, Mihael Kleine Boymann, "Phenol" in ncyclopedia of Industrial Chemistry, Wiley -VCH, 2004.
- 15. Peng T.Y. and Rocek, J. Am. Chem. Soc., 1976, 98, 1026-1032.
- 16. Das A.K., Co-ord. Chem. Rev., 2004, 81, 248-255.
- 17. Dyer J.R., Application of Absorption of Spectroscopy of Organic Compounds, Prentice-Hall, 1965.
- 18. Silverstein P.M. and Wester F.X, Spectrosopic Identification of Organic compounds, VI Ed., Wiley, 1998.
- 19. Karthikeyan G. Elango K.P. Karunakaran K. and Balasubramanian K., Oxid. Commun., 1998, 21(1), 51-56.
- 20. Chockalingam P. Ramakrishnan P.S. Arulraj S.J. and Nambi K., J. Indian Chem.Soc., 2002, 69, 247-252.
- 21. Venkatasubramanian, J. Sci. Ind. Res. Sec. B., 1961, 20, 541-548.
- 22. Amis E.S., Solvent Effects on Reaction Rates and Mechanism, Academic Press, New York, 1967, 42.
- 23. Palaniappan AN. Sekar K.G. and Ravishankar M., Oxid. Commun., 1998, 18, 52-57.
