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Kinetic and Mechanistic Profile of Some Phenolic Compounds by N-Chlorosaccharin in Aqueous Acid Medium

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ABSTRACT: We report the mechanistic approach of oxidation of some phenolic compounds such as catechol and cresol by N-chlorosaccharin in different compositions of acetic acid-water medium. The reaction is first-order with respect to oxidant and order varies from one to zero with respect to both [phenolic compounds] and [acid]. A positive effect of solvent establishes a positive ion-dipole interaction whereas added saccharin exhibits a negative effect on rate. Kinetic profile for consumption of fivefold of [NCSA] was obtained at reaction conditions which followed first-order kinetics, substantiated by unit slope evaluated from the parallel plot of log$_{10}$ (a-x) versus time plot. The stoichiometry of the oxidation is 2:1 demonstrating the formation of transitory complex between substrate and the protonated species of NCSA, which are readily oxidized to products. A plausible mechanism supported by substituent, abstraction of proton by Lewis base and temperature effect has been proposed.

Keywords: Catechol, Þ-cresol, N-chlorosaccharin, Kinetics, Oxidation

I. INTRODUCTION

The catechol (1,2-dihydroxybenzene) and Þ-cresol (4-methylphenol) are derivatives of phenol synthetically produced by the distillation of plant extract catechin and conventionally obtained from coal tar and by other methods too. These are consumed mainly as a precursor to pesticides, flavours and fragrances apart from that Þ-cresol is used industrially as antioxidant, because of being of relatively low toxicity and non-staining, including plastics, pharmaceuticals, dyes and more recently to create a breakthrough in manufacturing carbon nano-tubes at scales that are separated and not twisted. These phenolic compounds show hydrogen bonding (intermolecular/ intramolecular) in vis-à-vismesomeric, positive inductive and resonance effects. The elimination of proton of these compounds exhibits a very interesting properties like nitration, sulphonation, electrophilic substitution etc. which are used in medicinal and industrial dye stuffs chemistry. Though the scanty work on kinetics of oxidation of few phenolic compounds have been described recently in literature by bromamine-T [5,6].

N-chlorosaccharin has been introduced as an oxidimetric titrant [2] used in aqueous acetic acid medium. It is very stable in solid state and its solution in anhydrous acetic acid has better keeping qualities than most other oxidants of same type. In polar medium, it produces Cl^+ ion and H_2O^+Cl in acidic medium which are strong active species. The hidden potentiality of this moderant oxidant has not yet been widely realized only few reports [1,3,4,7,8,9,10] for the oxidation of compounds with this selective reagent are available. However, review of literature reveals that no systematic kinetic work has been documented with NCSA for phenolic compounds. The aim of investigation is to report the results of kinetic studies of catechol and Þ-cresol by NCSA in aqueous acetic acid medium.

II. EXPERIMENTAL

The reagents and solvents employed in the investigation were of AnalaR grade. The standardization of NCSA solution prepared in acetic acid (B.D.H.) after dissolving its requisite quantity in distilled water was carried out iodometrically. The solutions of two phenolic compounds viz. catechol: ($C_6H_4(OH)_2$, mol. wt.:110.11gm mol^{-1}, white crystal) and Þ-cresol (mol. formula $CH_3C_6H_4(OH)$, mol. wt.:108.14 gm/mol^{-1} colorless crystal), were made in freshly by dissolving their weighed amount in distilled water before installing experiments. The other necessary solutions of reagents (AG) pertaining to the investigation commercially used, were also prepared in standard form [12].

In kinetic probe, requisite quantity of oxidant (NCSA) solution was transferred into a reaction vessel while the solutions of substrate, acid and acetic acid with rest of water were taken separately in another vessel placed in a thermostatic water bath maintained at their experimental temperatures with an accuracy of $\pm 0.1^{\circ}$C. When, the duo solutions equilibrated and acquired the experimental temperature the reaction commenced by rapid addition of required amount of NCSA solution into the reaction mixture.

Immediately 2ml of aliquot was removed at regular intervals of time and reaction was monitored for disappearance of oxidant by titrating against sodium thiosulphate solution iodometrically [14]. The rate constant was evaluated by integral and graphical methods. The values of k_{obs} were reproducible in replicate runs within ± 3% precision.

III. RESULTS AND DISCUSSION

(a) The kinetic study was performed under the pseudo first-order condition

[substrate] >> [NCSA]

The stoichiometric estimation result in respect of unreacted NCSA was observed oxidant: substrate ratio as 2:1 as shown in equations.

The end-products (2,5-dichloro-1,6-dihydroxybenzene and 4-methyl-2,6-dichlorophenol) reactions as shown in equation (1) and equation (2) were separated from the extract and detected by modern methods. The study fails to establish the presence of free radicals when tested for reaction mixture with monomer poly acrylonitrile employing trapping method [11].

(b) The kinetic data for variation of five-times [NCSA] was obtained at reaction conditions follows first-order kinetics which is evidenced by unit slope evaluated from the parallel plot of $\log_{10}$ (a-x) versus time graph.

(c) The reaction rate follows nearly one to zero-order for catechol and cresol at their five-fold increase in concentrations (Table 1). The convincing evidence that these reactions are initiated by the formation of complex at transition state. Further authentication is authenticated by the verity of double reciprocal plots k^{-1} versus $[\text{substrate}]^{-1}$ which yielded positive intercepts on rate axis (Fig.1).

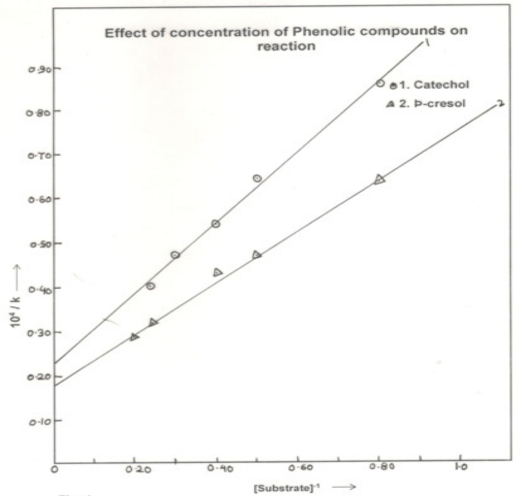
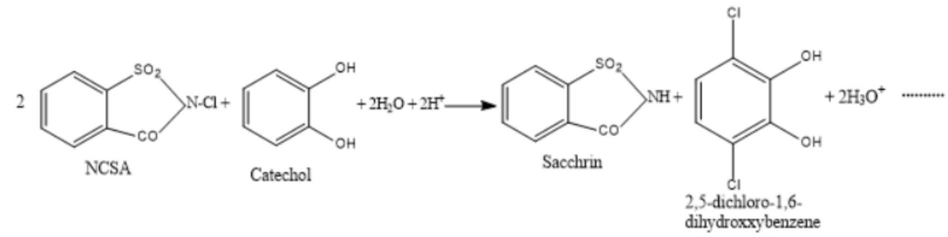


Fig. 1 Plot of k^{-1} vs. $[\text{Substrate}]^{-1}$
$10^3 \times$ [NCSA] (mol dm^{-3}) = 2.0 (1, 2) ; [H^+] (mol dm^{-3}) = 0.025 (1, 2) ; CH_3COOH-H_2O%, (v/v) = 30 (2), 40 (1) ; Temp. K = 308 (2), 313 (1)

Table 1: Dependence of rate on Substrates.

$10^3 \times$[NCSA] (mol dm^{-3}) = 2.0 (1, 2); [H^+] (mol dm^{-3}) = 0.025 (1, 2) ;CH_3COOH-H_2O, % (v/v) = 30 (2), 40 (1) ; Temperature K = 308 (2), 313 (1),

[Phenolic compound] × 10^2 (mol dm^{-3})	⟵ 10^4 k (sec^{-1}) ⟶	
	Catechol (1)	Þ-cresol (2)
1.25	1.16	1.55
2.00	1.55	2.09
2.50	1.86	2.32
3.33	2.12	-
4.00	2.61	3.17
5.00	3.03	3.58



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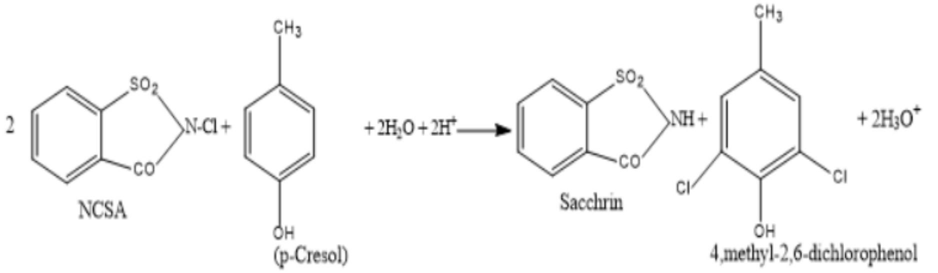


.... (2)

(d) The rate of oxidation was slightly retarded by varying five-times [H_2SO_4], showing fraction-order for it, evidenced by plots of k_{obs} vs. [H^+] (Fig. 2) as compiled in Table 2. The reactions is not acid catalysed.

Table 2: Dependence of rate [H_2SO_4]

10^3X [NCSA] (mol dm^{-3}) =2.0 (1,2);10^2×[substrate] (mol dm^{-3})= 2.50 (2). 3.33 (1) ;
CH_3COOH-H_2O %, (v/v) =30 (2), 40 (1); Temp. K =308 (2), 313 (1)

[H^+] (mol dm^{-3})	⟵ 10^4 k (sec^{-1}) ⟶	
	Catechol (1)	Þ-cresol (2)
0.025	2.12	2.32
0.050	2.03	2.22
0.10	1.92	2.18
0.20	1.65	1.90
0.25	1.49	1.77

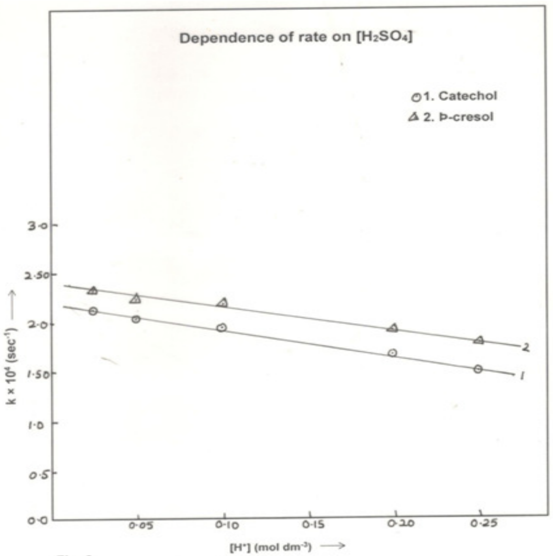
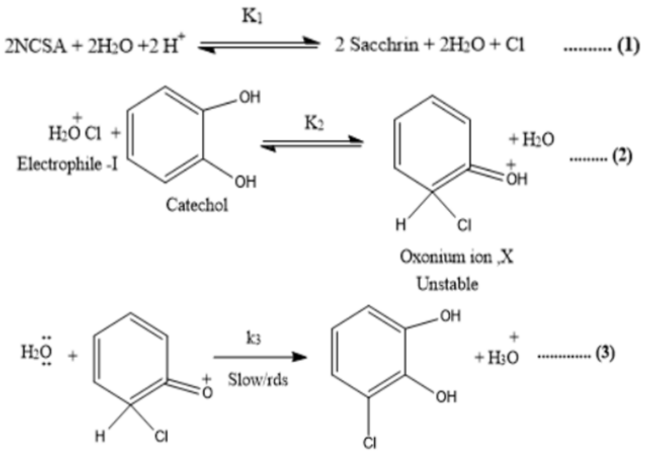


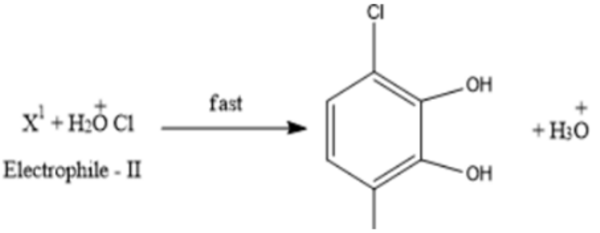
Fig. 2 Plot of k versus [H^+]

10^3×[NCSA](mol dm^{-3})= 2.00 (1,2); 10^2×[Substrate] (mol dm^{-3}) = 2.50(2),3.33 (1) ; CH_3COOH-H_2O%, (v/v) = 30 (2), 40 (1) ; Temp. K = 308 (2), 313 (1)

(e) The positive slope of the plots (logarithms of rate constant versus 1/D) give an idea about that positive dipole ion participates in reaction rate. The successive addition of neutral salt such as NaCl rules out the possibility of suppression in rate logically demonstrating insignificant effect. While, on the same note by addition of varying concentrations reductant product (saccharin) to the reaction mixture illustrates inhibition trend in reaction, ruling out completely its participation in the reaction mechanism.

Mechanism. Employing H_2O^+Cl as remote profile active species of oxidant (NCSA), A new scheme of mechanism supported by substituent and temperature effect has been proposed.

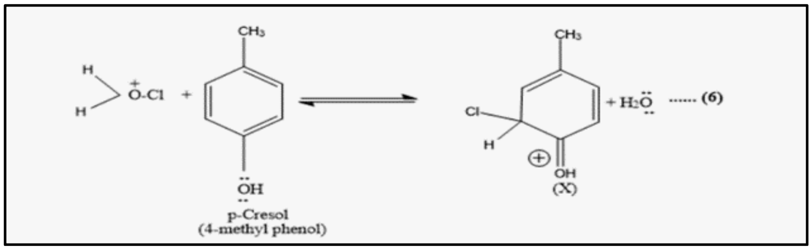


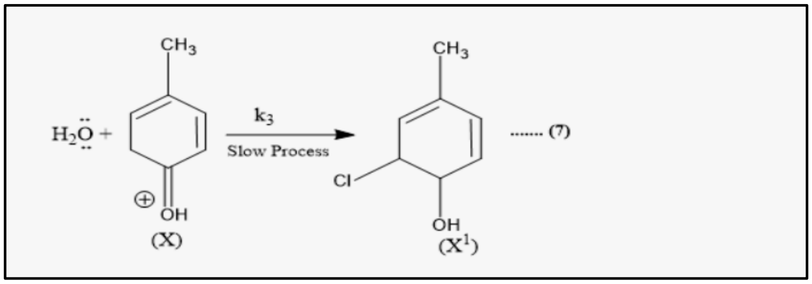


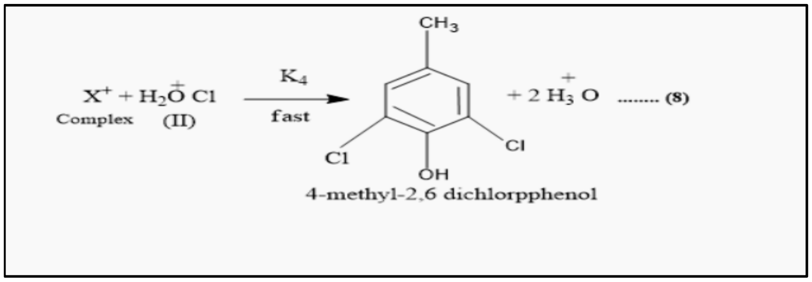
………. (4)

$$2H_3\overset{+}{O} \rightleftharpoons H_2O + 2H^+ \qquad ………. (5)$$

Mechanism of p-cresol. Considering the various steps involved in the almost common mechanism of catechol and p-cresol and imposing the condition of steady state approximation, the final rate expression was derived as:







Considering the various steps involved in the almost common mechanism of catechol and p-cresol and imposing the condition of steady state approximation, the final rate expression was derived as:

$$\mathbf{k_{obs}} = \frac{\mathbf{k_1 k_2 k_3 [NCSA]\,[H^+]\,[Subs.]}}{\mathbf{1 + K_1[H^+] + K_1K_2[SUBS.]\,[H^+]}} \qquad \ldots\ldots\ldots\ldots(9)$$

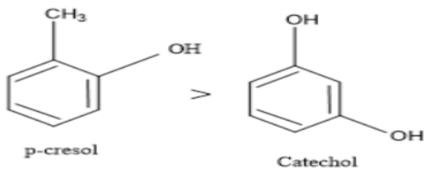
On transformation of equation (9) to equation (10), we get

$$\frac{\mathbf{1}}{\mathbf{k_{obs}}} = \frac{\mathbf{1}}{\mathbf{K_2K_1[Substrate\,]}}\left\{\frac{\mathbf{1}}{\mathbf{K_1[H^+]}} + \mathbf{1}\right\} + \frac{\mathbf{1}}{\mathbf{k_3}} \qquad \ldots\ldots\ldots\ldots(\mathbf{10})$$

The rate is in good proximity with the experimental results and explains all the facts including existence of complex at different conditions.

Reactivity and Structure

In present context of the study assessed the reactivity



The presence of –OH group at different position of compounds along with substituent group i.e., design of molecules plays vital role in dealing the reactivity the methyl group of cresol that exhibit + I effect.

Table 3: Thermodynamic and activation parameters for the reaction between Phenolic compounds and NCSA.

Substrate	$\Delta Ea^{\#}$ kJ / mol	$\Delta H^{\#}$ kJ / mol	$\Delta S^{\#}$ JK^{-1} / mol^{-1}	$\Delta F^{\#}$ kJ / mol
Catechol	65.43	62.02	-89.33	90.29
Þ-cresol	59.28	53.89	-109.11	86.94

The hydroxyl group through delocalisation of electron cloud developed on the phenoxide anion helps to stabilize the molecule and consequently accelerate the rate of oxidation. The abstraction of the proton by the lewis base checks down the reaction rate in the rate determining step and moreover the hydroxyl groups located at different positions in catechol retard the rate **Comparatively.** The sequence of above order of reactivity trend is also well supported by the Arrhenius parameters displayed in Table 3. The value of Ea (59.28 kJ/mole) is lowest for most reactive compound p-cresol where as it is 65.43 kJ mole^{-1} for catechol. The identical mechanism prevails in them as the values of $\Delta G^{\#}$ are almost found in the vicinity of 86.94 to 90.29 kJ mole^{-1}and fairly positive values of $\Delta H^{\#}$ (53.89 to 62.02 kJ mole^{-1}) favours the highly solvated nature of transition state [13]. The high negative values of entropies of activation ($-\Delta S^{\#}$= 89.33 to 109.11 JK^{-1} mole^{-1}) evidenced that even highly ordered transitory complex is formed.**[15]**Overall, the observation reveals that reactions are enthalpy controlled.

IV. CONCLUSION

The protonated form of active species $[H_2O^+Cl]$ which participates in the reaction to form complex at transition state was established. The stoichiometry (oxidant: phenolic compounds ratio) was determined as 2:1. The disproportionation of intermediate compounds occurs in the slow process to yield the products. The incline of the plots (logs of k vs 1/D) gives evidence that positive dipole ion chip in the reaction rate. The addition of neutral salt for instance NaCl rules out the possibility of inhibition in rate, rationally signifying insignificant effect. Though, by addition of varying concentration of reductant product (saccharin) to the reaction mixture illustrates reticence trend in reaction, ruling out completely its participation in the reaction mechanism. The mechanism of substrates involved abstraction of proton and molecules stabilized by delocalisation and also order of reactivity supported by thermodynamic parameters was discussed. The applied aspects of the work may be utilized in plastic pharmaceuticals, and industrial dye stuffs chemistry.

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Conflict of Interest: The writers of this manuscript do hereby declare no conflict of interest.

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