

# KINETICS OF OXIDATION OF P-PHENYLENE DIAMINE BY 2,6-DICHLORO QUININE-4-CHLORO-IMIDE

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**Abstract:** Gibbs reagent 2,6-dichloroquinone -4-chloro-imide (DCQCI) has been utilised for the estimation of phenols and pyridoxine for a quite number of years. Para-phenylene diamine (p-PDA) having two (1,4)-diamino functions attached to a benzene nucleus is well known to undergo a variety of oxidation or oxidative hydrolytic reactions in the presence of electron acceptors. The investigation mainly deals with the oxidation of p-phenylene diamine in aqueous AcOH - HClO<sub>4</sub> mixtures by 2,6-dichloroquinone-4-chloro-imide. The reaction is found to be first order in oxidising agent. The reaction is found to be second order in substrate. The reaction rate decreases with increasing the concentration of perchloric acid.

The most probable mechanistic scheme envisaged is that precursor intermediate complex being formed between the oxidant species and a molecule of unprotonated substrate species which in a rate determining step condenses with another molecule of the substrate to give intermediate product which in fast step gives final product.

**Introduction and Scope:** Gibbs reagent 2,6-dichloroquinone -4-chloro-imide (DCQCI) has been utilised for the estimation of phenols and pyridoxine for a quite number of years. The main reaction has been a coupling process leading to colour changes and thus colorimetry was extensively used for the assay of these compounds. Para-phenylene diamine (p-PDA) having two (1,4)-diamino functions attached to a benzene nucleus is well known to undergo a variety of oxidation or oxidative hydrolytic reactions in the presence of electron acceptors. The actual products of the reaction depend upon the reaction conditions employed: concentration, the nature of the oxidant, the acidity of the medium, the solvent system besides the relative ratios of the oxidant and substrate concentrations. The reactions of para-phenylene diamine are very complicated due to the availability of two donor nitrogen sites, and due to the subsequent reactions of the intermediate products not to mention of the additional complication of electrophilic attack at the nitrogen sites and at the nucleus.

**P-Phenylene Diamine:** The investigation mainly deals with the oxidation of p-phenylene diamine in aqueous AcOH - HClO<sub>4</sub> mixtures by 2,6-dichloroquinone-4-chloro-imide.

**a) Dependence on Oxidant:** The reaction is found to be first order in oxidising agent. Plot of log(a-x) vs time is linear up to three half lives of the reaction indicating first order dependence on oxidising agent. The kinetic data is given in Table 1.

**Table 1**

Variant	[Variant] x 10 <sup>4</sup> M	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>
DCQCI	2.5	10.7
	5.0	9.2
	10.0	10.1

**b) Dependence on Substrate:** The reaction is found to be second order in substrate. Plot of  $\log k_1$  vs  $\log [S]$  is linear with slope two indicating second order dependence. The observation that the plot of  $\frac{[S]}{k_1}$  vs  $\frac{1}{[S]}$  is linear and passes through origin also confirms the second order dependence on substrate. Such second order dependence has been observed in the oxidation of p-phenylene diamine with  $I_3^-$ . The kinetic data is given Table -2.

**Table 2:**

Variant	[Variant] x 10 <sup>3</sup> M	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>
p-phenylene diamine	3.1	0.25
	6.2	1.56
	12.5	9.23
	25.0	47.74

[DCQCI] = 5.0 x 10<sup>-4</sup> M      [H<sup>+</sup>] = 0.1 M  
AcOH - H<sub>2</sub>O = 10% - 90%(v/v)      Temp = 35°C

**c) Dependence on Acid Concentration:** The reaction rate decreases with increasing the concentration of perchloric acid. The reaction is found to be inverse mixed order. Plot of  $\log k_1$  vs  $\log [H^+]$  is linear with a slope of 1.5. Plot of  $k_1 [H^+]$  vs  $\frac{1}{[H^+]}$  gives an intercept and slope. The intercept corresponds to first order component and slope corresponds to second order component. This explains the observed mixed order kinetics. The combination of first order kinetics and second order kinetics giving inverse dependence on  $[H^+]$  gives resultant inverse 1.5 order on  $H^+$ . The kinetic data is given in Table: 3.

**Table 3:**

Variant	[Variant] x 10 <sup>2</sup> M	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>
HClO <sub>4</sub>	5.0	33.2
	10.0	9.2
	20.0	6.0
	40.0	1.6

[DCQCI] = 5.0 x 10<sup>-4</sup> M      [p-PDA] = 12.5 x 10<sup>-3</sup> M  
AcOH - H<sub>2</sub>O = 10% - 90% (v/v)      Temp = 35°C

**Effect of Varying Solvent Composition:** The reactions have been carried out at varying solvent compositions to find the effect of change in dielectric constant. The reaction rate decreases with increase in concentration of acetic acid. This reaction essentially involves  $H_2OCl^+$  and the dipolar molecule of the amine. This requires an increase in rate with decrease in dielectric constant. But the observation is reverse. Thus specific solvent effects probably are causing this observation. Probably the following factors like solvation, acidic or basic nature of the solvent, effect of solvent on molecular dispersion, non random distribution of the component of mixed solvent are responsible. Plot of  $\log k_1$  vs  $\frac{1}{D}$  is linear (Fig.6). The kinetic data is given in Table-4.

**Table 4:**

Variant	% of Variant	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>
AcOH	5	10.5
	10	9.2
	20	6.1
	40	4.5

[DCQCI] = 5.0 x 10<sup>-4</sup> M      [H<sup>+</sup>] = 0.1 M  
[p-PDA] = 12.5 x 10<sup>-3</sup> M      Temp = 35°C

**Effect of Temperature:** The reactions are carried out at three different temperatures i.e., 35°C, 45°C and 55°C to compute various activation parameters. Plot of  $\log k_1$  vs  $\frac{1}{T}$  is linear (Fig.7). The kinetic data is given in Table-5.

**Table 5:**

Variant	Change in Variant °C	$k_1 \times 10^2 \text{ min}^{-1}$
Temperature	35	9.2
	45	13.8
	55	29.0

[DCQCI] =  $5.0 \times 10^{-4}$  M      [H<sup>+</sup>] = 0.1 M  
 [p-PDA] =  $12.5 \times 10^{-3}$  M      AcOH - H<sub>2</sub>O = 10% - 90% (v/v)

The derived Arrhenius parameters are given in Table 6.

**Table 6:**

**Arrhenius Parameters at 308°K:**

Compound	$\Delta E^\ddagger$ KJ/mole	$\Delta H^\ddagger$ KJ/mole	$-\Delta S^\ddagger$ JK <sup>-1</sup> / mole	$\log_{10} P_Z$	$\Delta G^\ddagger$ KJ/mole.
p-phenylene diamine	44.18	41.4	130.44	6.45	81.65

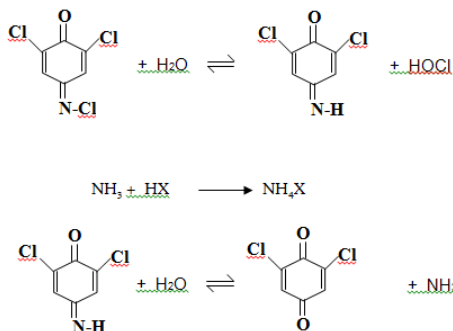
The kinetic features and net activation parameters do not provide any clue whether or not this reaction involves termolecular interactions.

In as much the oxidant DCQCI is well known to function as a two electron oxidant. It is reasonable to assume that this reaction does not go through step wise one electron transfer which would mean that this reaction should go through radical path way. It appears that this mechanistic speculation involving radicals would impose large energy barrier, since a large number of nuclei-rearrangement should be required for radical formation and hence it is most unlikely that this reaction would proceed through radical path way.

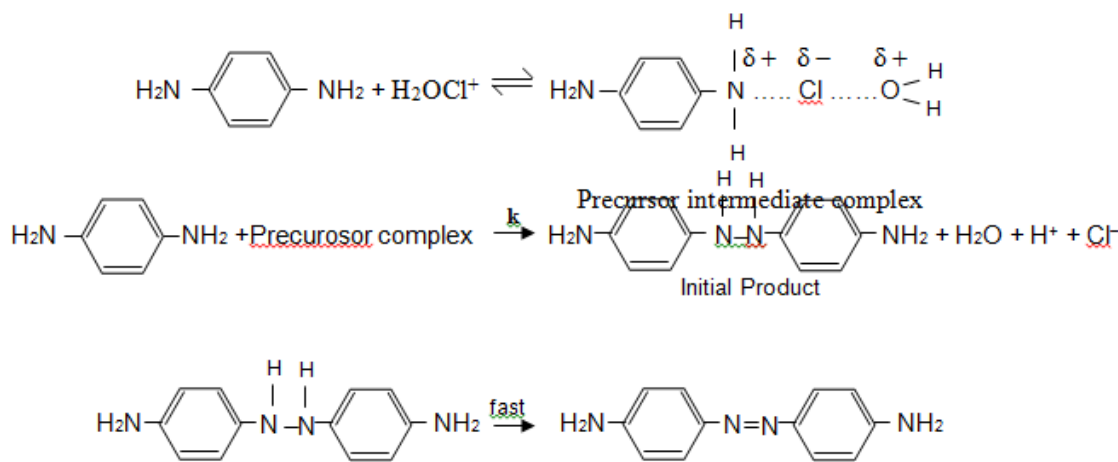
The possibility that the rapid electron transfer from one of the substrate species to the oxidant species followed by rate determining condensation of the redox intermediate thus produced with the second substrate species is also unlikely as this mechanistic supposition would involve too many ionic species in an equilibrium step, and there should be much larger retardation with increase in H<sup>+</sup> than what has been observed experimentally.

**Mechanism and Rate Law:** The most probable mechanistic scheme envisaged is that precursor intermediate complex being formed between the oxidant species and a molecule of unprotonated substrate species which in a rate determining step condenses with another molecule of the substrate to give intermediate product which in fast step gives final product.

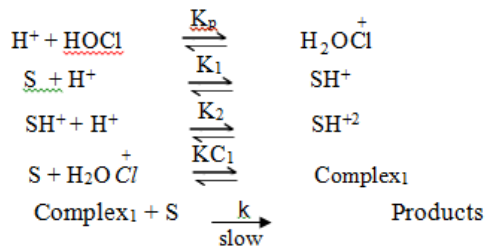
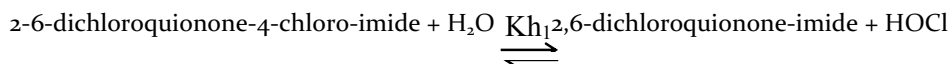
The sequence of reactions may be represented as follows.



The most active species  $H_2OCl^+$  produced in first hydrolytic step. The mechanistic path way involving the main oxidant species and substrate are given below.



The relevant rate law is derived as follows. The sequence of reactions of hydrolysis of DCQCI are given below.



$$\begin{aligned}
 \therefore \text{Rate} &= k [C_1] [S] \\
 &= k.K_C.[S] [S] [H_2OCl^+] \\
 &= k.K_C.K_p [S]^2 [H^+] [HOCl] \\
 S_T &= S + SH^+ + SH^{+2} \\
 &= S + K_1 [S] [H^+] + K_1.K_2[S] [H^+]^2 \\
 &= S [1 + K_1H^+ + K_1K_2 [S] [H^+]^2] \\
 &\text{by neglecting Square terms} \\
 S_T &= S [1 + K_1H^+] \\
 \therefore \text{Rate} &= \frac{kK_C K_p [S_T]^2 [HOCl] [H^+]}{[1 + K_1H^+]^2} \\
 &= \frac{kK_C K_p [S_T]^2 [HOCl] [H^+]}{[1 + 2K_1H^+ + K_1H^+{}^2]} \\
 &= \frac{kK_C K_p [S_T]^2 [HOCl]_T [H^+]}{[1 + 2K_1H^+ + K_1H^+{}^2] [1 + K_pH^+]}
 \end{aligned}$$

Replacing  $[HOCl]_T$  by DCQCI

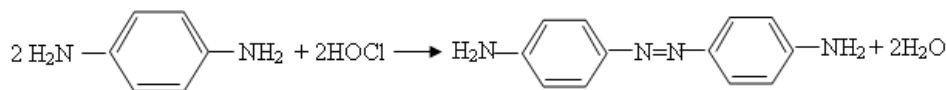
$$\therefore \text{Rate} = \frac{K_h k K C_1 K_p [S_T]^2 [DCQCI] [H^+]}{\{1 + 2K_1 H^+ + K_1 H^{+2}\} \{1 + K_p H^+\}}$$

If  $1 < K_p H^+$  neglecting the second term in the denominator we get

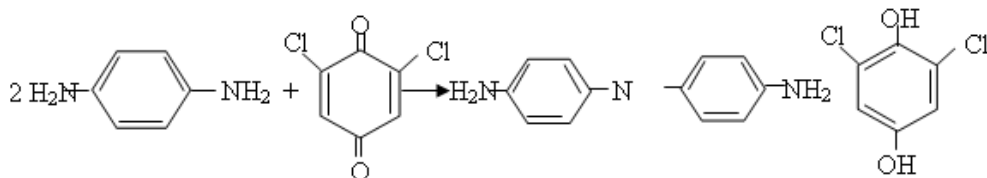
$$\therefore \text{Rate} = \frac{k K C_1 [S_T]^2 [DCQCI]}{\{1 + 2K_1 H^+ + K_1 H^{+2}\}}$$

The rate law explains the observed first order in oxidant, second order in substrate, and a mixed order in  $H^+$  involving both first order component of  $H^+$  and second order component in  $H^+$  resulting in inverse 1.5 order in  $H^+$ .

**Stoichiometric Studies:** The product studies under the given set of conditions were performed and worked up as follows. The ratio of substrate-oxidant was maintained as 1:10. The reactants were mixed and the mixture was allowed to react over night. It has been found that two oxidant species HOCl and 2,6-dichloro benzoquinone interact causing oxidation to the products in a ratio 2:1 indicating that both the species interact finally giving.



Similarly



The experimental procedure is as follows.

The contents were treated with solid sodium bicarbonate until there was no evolution of carbon dioxide gas. The resultant mixture was extracted with diethyl ether, the solvent was evaporated from the ether layer and a minimum quantity of dilute HCl was added (pH ~ 3).

The green colour solution was evaporated over a water bath to get a dirty green solid. This crude product was crystallized from absolute ethanol and filtered. The HCl from this salt was neutralized by treatment with a saturated solution of  $\text{NaHCO}_3$ , the green solid was filtered, washed well with water, recrystallised from absolute ethanol, vacuum-dried and desiccated.

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