

CHEMICAL KINETICS AND CATALYSIS

Kinetics of Oxidation of Aniline, *p*-Aminobenzoic Acid, and *p*-Nitroaniline by 2,6-Dichloroquinone-4-Chloro-Imide¹

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Abstract—The kinetics of the oxidation of aniline, *p*-aminobenzoic acid, and *p*-nitroaniline by 2,6-dichloroquinone-4-chloro-imide was studied in aqueous acetic acid. The reaction was found to be consecutive: the first stage was oxidation by HOCl (the hydrolytic product obtained from 2,6-dichloroquinone-4-chloro-imide), and the second stage was oxidation of aniline by 2,6-dichloroquinone. The reactions were found to be first order in the oxidant and first order in the substrate. The reaction was independent of $[H^+]$ in the range studied using $HClO_4$ for *p*-aminobenzoic acid and *p*-nitroaniline. A slight inverse dependence on $[H^+]$ was observed with aniline, for which changes in pH resulted in reaction acceleration. The reactions were not susceptible to changes in pH as observed in the acetic acid–sodium acetate buffer media in the case of *p*-aminobenzoic acid and *p*-nitroaniline. The primary products were the corresponding hydrazobenzenes, which finally yielded azobenzene. A suitable mechanism was postulated to explain the results.

Recently, the kinetics of the oxidation of the thiocyanate ion by 2,6-dichloroquinone-4-chloro-imide has been reported [1]. This communication deals with the oxidation of aniline, *p*-aminobenzoic acid, and *p*-nitroaniline by this new oxidizing agent.

EXPERIMENTAL

2,6-Dichloroquinone-4-chloro-imide: a Fluka (purum grade) sample was used to make the stock solution in glacial acetic acid. Aniline, *p*-aminobenzoic acid, and *p*-nitroaniline: BDH AnalaR samples were used after aniline was distilled and *p*-aminobenzoic acid and *p*-nitroaniline were recrystallized. All other chemicals, acids, solvents used in these investigations were of analytical reagent grade.

Kinetic method: aliquots of the reaction mixture were analyzed by the iodometric method. The reaction mixture containing 2,6-dichloroquinone-4-chloro-imide (5.0 ml) was pipetted out at various intervals of time into a mixture of a iodate-free potassium iodide solution containing dilute sulphuric acid (2 N) in a carbon dioxide atmosphere. The liberated iodine was titrated against the standard thiosulfate solution to the disappearance of the blue starch–iodine end point.

RESULTS AND DISCUSSION

The following facts emerge from the kinetic data:

The Aniline–2,6-Dichloroquinone-4-Chloro-Imide System

(1) In 100% acetic acid, the reaction is exclusively the oxidation of aniline by 2,6-dichloroquinone-4-chloro-

imide. This implies that the N-halo compound does not undergo hydrolysis in this medium and the reaction is only oxidation of aniline by unhydrolyzed 2,6-dichloroquinone-4-chloro-imide. Boric acid does not accelerate the rate of the reaction.

(2) In aqueous acetic acid, the reaction involves two steps:

(a) oxidation of aniline by the product of hydrolysis of 2,6-dichloroquinone-4-chloro-imide, which is HOCl;

(b) concurrent oxidation of aniline by 2,6-dichloroquinone, the other hydrolytic product of 2,6-dichloroquinone-4-chloro-imide.

In addition, it appears that the interaction of 2,6-dichloroquinone-4-chloro-imide with aniline gives indoaniline as a minor product in this medium. This is substantiated by carrying out the reaction in the presence of boric acid. It has been found earlier in the work on substituted phenols like pyridoxine and 2,6-dichloroquinone-4-chloro-imide that the coupling reaction leading to indophenol formation is suppressed in the presence of boric acid [2]. This was explained by complex formation between the –OH and –CH₂OH groups and boric acid; as a result, the position *para* to the phenolic group is not activated for the coupling reaction to occur with 2,6-dichloroquinone-4-chloro-imide. The origin of acceleration observed with aniline in the presence of boric acid is very much different, as there are no vicinal hydroxyl groups in aniline. But the tendency of nitrogenous compounds like pyridine, quinoline, and isoquinoline to form borates with boric acid seems to be applicable to aniline as well, because the pK_a values of all these bases are similar. These borates are formed independent of reaction temperatures in the range 0–115°C [3].

¹ This article was submitted by the authors in English.

Table 1. Oxidation of aniline by 2,6-dichloroquinone-4-chloro-imide at substrate concentrations exceeding that of the oxidant

Variable component	Variable component concentration	$k_1 \times 10^5, s^{-1}$	$k_1' \times 10^5, s^{-1}$
Oxidant (0.015 M aniline)	0.00025 M	29.30	24.27
	0.0005 M	28.78	25.73
	0.001 M	31.36	26.83
Aniline	0.0025 M	5.75	4.69
	0.005 M	10.22	8.10
	0.01 M	21.87	16.81
	0.015 M	28.78	25.73
AcOH	5%	32.61	27.14
	10%	20.15	14.71
	20%	10.22	8.10
	40%	2.34	1.83
Sodium acetate	0.01 M	7.52	4.31
	0.02 M	10.22	8.10
	0.05 M	14.64	11.47
	0.10 M	27.06	17.52
	0.20 M	40.03	25.25
Temperature (0.05 M NaOAc)	40°C	14.64	11.47
	50°C	26.48	17.51
	60°C	78.57	25.88
HClO ₄ (5% AcOH)	0.0001856 M	16.92	12.26
	0.0003712 M	15.70	12.40
	0.0030224 M	12.66	9.02
	0.0060488 M	8.45	6.66
Variation of medium	[HClO ₄] = 7.5×10^{-4} M	[Aniline] = 5×10^{-3} M	[Oxidant] = 5×10^{-4} M
	20% AcOH	6.21	3.58
	20% EtOH	52.39	36.72

Note: Reaction conditions: [2,6-dichloroquinone-4-chloro-imide] = 5×10^{-4} M; [aniline] = 5×10^{-3} M; [AcOH] = 20%; [sodium acetate] = 0.02 M; $T = 40^\circ\text{C}$.

If this is true, then obviously, the *para* position of aniline in the presence of boric acid will not be activated for the coupling reaction to occur. Thus, there will be more of availability of aniline molecules for the main oxidation process to occur leading to the formation of hydrazobenzenes and finally azobenzenes as products. Azobenzenes as products have been reported earlier by many workers for the oxidation of aniline by lead tetraacetate [4, 5], chloramine-T [6], and thallium(III) [7]. Hence, boric acid causes acceleration with pyridoxine and aniline for different reasons. But the common factor is the absence of the coupling reaction with 2,6-dichloroquinone-4-chloro-imide at the *para* position of the substrate. Extensive work by Robinson [3] has established that organic bases like pyridine, quinoline and isoquinoline form borates with boric acid. These borates have been subjected to an X-ray diffraction study, and their identity and structure have

been established. Hence, the same argument is involved as stated earlier for interaction of boric acid with aniline whose basicity is similar to that of quinoline. Thus, the acceleration observed in the presence of boric acid with aniline is reasonably explained. To buttress our arguments further, there is no coupling reaction in 100% acetic acid, and this is confirmed by the absence of acceleration in the presence of boric acid with 100% acetic acid. So, it is quite clear that boric acid enhances the rate by suppressing the coupling process of indoaniline formation and making more aniline molecules available for oxidation by 2,6-dichloroquinone-4-chloro-imide.

(3) The kinetic orders observed are: first order in aniline and first order in the oxidant.

The reaction rate decreased with an increase in the percentage of acetic acid and increased with the concentration of sodium acetate (Tables 1, 2). This shows

Table 2. Oxidation of aniline by 2,6-dichloroquinone-4-chloro-imide at substrate concentrations lower than that of the oxidant

Variable component	Variable component concentration	$k_1 \times 10^5, s^{-1}$	$k_1' \times 10^5, s^{-1}$
Oxidant	0.0005 M	2.58	
	0.0010 M	3.03	
	0.0015 M	2.76	
Aniline	0.000625 M	0.16	
	0.000125 M	0.34	
	0.00025 M	0.75	
	0.0005 M	2.58	
	0.00075 M	4.53	1.68
	0.0010 M	6.75	2.20
	0.0015 M	7.33	5.43
AcOH	0.0020 M	11.07	8.03
	5%	2.58	
	10%	1.28	
	20%	0.80	
Sodium acetate	40%	0.25	
	0.02 M	2.58	
	0.05 M	3.65	
	0.10 M	4.92	
HClO ₄	0.20 M	9.21	
	0.0007561 M	1.30	
	0.0030228 M	0.94	

Note: Reaction conditions: [2,6-dichloroquinone-4-chloro-imide] = 5×10^{-4} M; [aniline] = 5×10^{-4} M; [AcOH] = 5%; [sodium acetate] = 0.02 M; $T = 40^\circ\text{C}$.

Table 3. Oxidation of *p*-aminobenzoic acid by 2,6-dichloroquinone-4-chloro-imide

Variable component	Variable component concentration	$k_1 \times 10^5, s^{-1}$	$k_1' \times 10^5, s^{-1}$
Oxidant (0.015 M <i>p</i> -aminobenzoic acid)	0.00025 M	19.28	8.56
	0.0005 M	15.78	8.87
	0.001 M	17.22	9.72
	0.0015 M	17.44	10.91
	0.0025 M	3.01	1.54
<i>p</i> -Aminobenzoic acid	0.0025 M	3.01	1.54
	0.005 M	5.74	4.42
	0.02 M	10.02	7.04
	0.015 M	15.78	8.87
	5%	8.25	6.07
AcOH	20%	5.74	4.42
	40%	1.45	1.01
	0.01 M	5.72	3.705
Sodium acetate	0.02 M	5.74	4.42
	0.05 M	6.09	4.54
	0.10 M	7.85	5.74
	0.20 M	8.76	5.57
	0.30 M	8.98	5.28
	40°C	6.09	4.54
Temperature (0.05 M NaOAc)	50°C	14.07	7.89
	60°C	20.05	11.1
	0.00075 M	4.59	2.68
HClO ₄	0.0015 M	5.38	2.03

Note: Reaction conditions: [2,6-dichloroquinone-4-chloro-imide] = 5×10^{-4} M; [substrate] = 5×10^{-3} M; AcOH = 20%; [sodium acetate] = 0.02 M; $T = 40^\circ\text{C}$.

that it is a dipole-dipole reaction, and it is susceptible to changes in pH. The reaction rate is composed of only one step of oxidation when the oxidant concentration is higher than the concentration of substrate and when they are equal. When the concentration of substrate is higher than that of the oxidant, the rate is composed of two steps as the reaction goes to completion since all the oxidant is consumed. A stoichiometry of 2 : 1 is observed. This is confirmed by a series of experiments conducted in the range 6.25×10^{-5} – 5×10^{-4} M aniline at a constant concentration of 5×10^{-4} M 2,6-dichloroquinone-4-chloro-imide. The reaction virtually stops at varying degree (6–50%) of oxidant consumption in experiments with 6.25×10^{-5} to 5×10^{-4} M aniline and 5×10^{-4} M 2,6-dichloroquinone-4-chloro-imide concentrations.

The reaction rate decreases when the concentration of HClO₄ increases, though the decrease is not very large (twice for a thirty times increase in HClO₄) signifying that the reactive molecules are free aniline molecules. When the medium is changed from 20% acetic

acid to 20% ethyl alcohol, the reaction is accelerated. The rate of the first step of oxidation is higher than the rate of the second step of oxidation, which appears to be reasonable as the redox potentials of the hydrolyzed forms of HOCl and 2,6-dichloroquinone-4-chloro-imide are different.

The *p*-Aminobenzoic Acid-2,6-Dichloroquinone-4-Chloro-Imide System

In the case of *p*-aminobenzoic acid, the following facts are observed:

- (1) The reaction is first order in the oxidant.
- (2) The reaction is first order in the substrate (*p*-aminobenzoic acid).

The reaction is independent of the concentration of sodium acetate; this is also confirmed by the independence from an increase in the concentration of perchloric acid. The reaction rate decreases with an increase in the percentage of acetic acid. Essentially, the reactions

are two-step processes in an aqueous medium as observed with aniline:

(a) the oxidation of *p*-aminobenzoic acid by the hydrolysis product HOCl;

(b) the oxidation of *p*-aminobenzoic acid by 2,6-dichloroquinone, which is the other hydrolysis product.

The *p*-Nitroaniline-2,6-Dichloroquinone-4-Chloro-Imide System

Similar orders have been observed with *p*-nitroaniline. The reaction is first order in the oxidant and first order in the substrate. The reaction is not susceptible to an increase in the concentration of sodium acetate and to an increase in the concentration of perchloric acid. The reaction rate decreases as the percentage of acetic acid increases.

STRUCTURE AND REACTIVITY

It has been observed that the rate decreases as we proceed from aniline to *p*-nitroaniline (Tables 2-4). The order of reactivity is aniline > *p*-aminobenzoic acid > *p*-nitroaniline.

The plot of $\log k$ versus σ is virtually linear, indicating that the electron deactivating groups decrease the reaction rate. It has been observed that, in 100% acetic acid, the oxidation of aniline by 2,6-dichloroquinone-4-chloro-imide (A) itself occurs.

In the aqueous system, two processes occur:

- (1) oxidation of aniline by HOCl and
- (2) oxidation of aniline by 2,6-dichloroquinone.

The kinetic rates of the second reaction are distinctly much lower than the kinetic rates of the first process of the oxidation of aniline and *p*-aminobenzoic acid. In the case of *p*-nitroaniline, the reactions are strongly retarded. The first oxidation stage rate is slightly higher than the rate of the second stage. The trends are clear in all cases. But the degree of a decrease in the rate is much lesser in the case of *p*-nitroaniline. It may be appropriate to say that, when the substrate is very much deactivated (σ being +0.778) as in the case of *p*-nitroaniline, the kinetic rates observed with HOCl and 2,6-dichloroquinone do not clearly indicate the different capacities of the two diverse oxidizing species, namely, HOCl and 2,6-dichloro-*p*-benzo-quinone, though the trends are clear. With aniline and *p*-aminobenzoic acid, the difference in the rates clearly brings out the different capacities of the two oxidizing species, the first step of oxidation by HOCl being faster than the second step of oxidation by 2,6-dichloro-*p*-benzo-quinone (B).

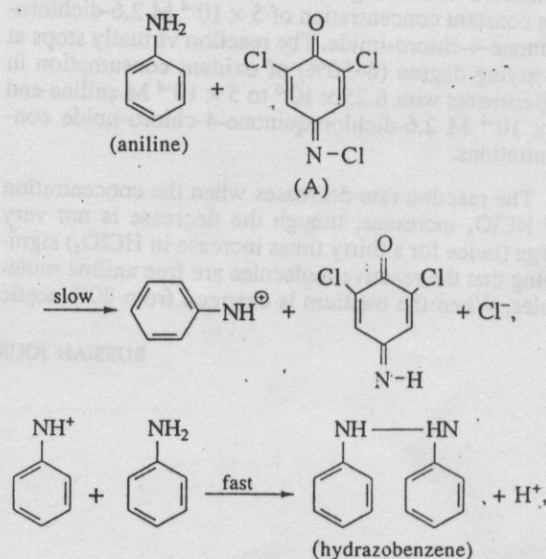
Table 4. Oxidation of *p*-nitroaniline by 2,6-dichloroquinone-4-chloro-imide

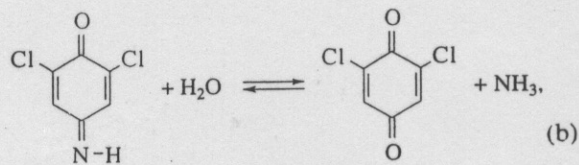
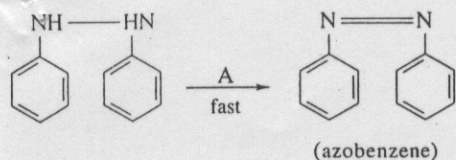
Variable component	Variable component concentration	$k_1 \times 10^5$, s ⁻¹	$k_1' \times 10^5$, s ⁻¹
Oxidant (0.015 M <i>p</i> -nitroaniline)	0.00025 M	0.94	0.9
	0.0005 M	1.17	1.00
	0.001 M	1.35	1.28
	0.0015 M	1.51	1.40
	0.005 M	0.43	0.39
<i>p</i> -Nitroaniline	0.010 M	0.75	0.70
	0.015 M	1.17	1.00
	0.02 M	1.5	1.40
	0.02 M	1.5	1.40
AcOH	5%	1.01	0.94
	10%	0.71	0.69
	20%	0.43	0.39
Sodium acetate	0.02 M	0.43	0.39
	0.05 M	0.42	0.38
	0.10 M	0.47	0.41
	0.10 M	0.47	0.41
Temperature (0.15 M <i>p</i> -nitroaniline)	40°C	1.17	1.00
	50°C	1.75	1.67
	60°C	3.13	2.94
HClO ₄	0.00075 M	0.58	0.50
	0.0015 M	0.64	0.43

Reaction conditions: [2,6-dichloroquinone-4-chloro-imide] = 5×10^{-4} M; [substrate] = 5×10^{-3} M; AcOH = 20%; [sodium acetate] = 0.02 M; T = 40°C.

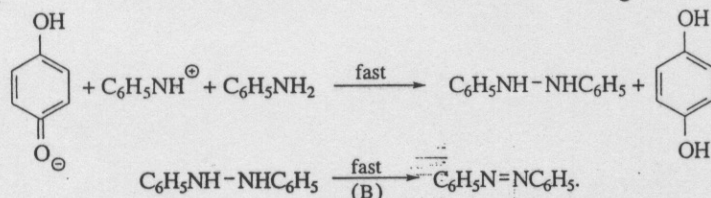
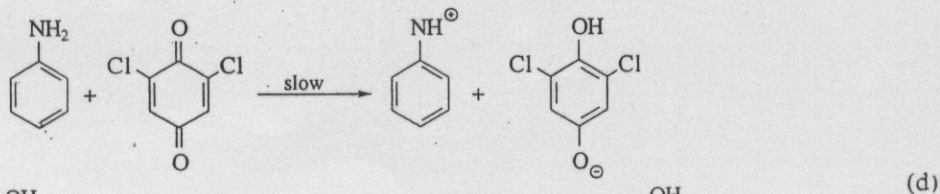
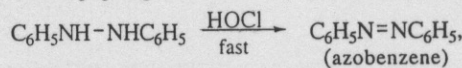
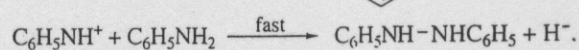
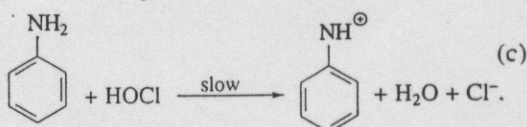
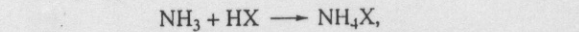
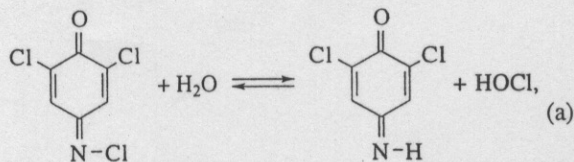
THE MECHANISM OF REACTION

In a non-aqueous medium:

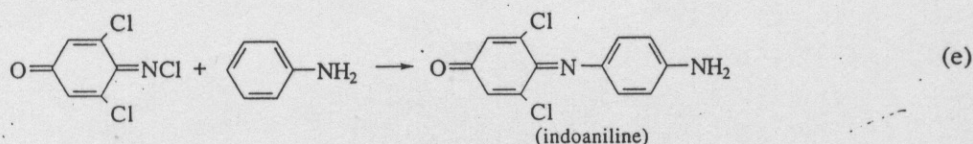




In an aqueous medium:



The side reaction that occurs in the aqueous system is as follows:



The above mechanistic sequences explain the formation of products both in aqueous and non-aqueous media. The reaction route involves electron transfer at the rate-determining step giving RNH^+ , which, at the fast stage, gives hydrazobenzene. Finally, hydrazobenzene is converted into azobenzene at the final stage. The observed ρ value of -3.25 is evidence for such a rate-determining step involving an ionic path. This negative ρ value suggests that the electron withdrawing groups retard the process.

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