

# KINETICS AND MECHANISM OF AERIAL OXIDATION OF HYDROQUINONE IN A DEVELOPER SOLUTION AND DETERMINATION OF DEVELOPER'S HALF-LIFE AT 20°C

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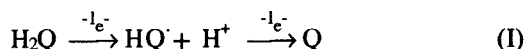
## Abstract

The aerial oxidation of hydroquinone in a freshly prepared developer solution at 20°C has been studied through the measurement of concentration changes by a spectrophotometric method. The concentration of consumed hydroquinone is directly proportional to time, and the equation  $t_{1/2} = C_0 / 0.0786$  was obtained to calculate the half-life of the developer. In this equation, the half-life is in hours and the initial concentration of hydroquinone,  $C_0$ , is in g/l. The following mechanism for the reaction has also been proposed.

## Introduction

Hydroquinone, or 1,4-dihydroxybenzene ( $H_2Q$ ), is the main component of the majority of black-and-white developers. This compound is oxidized by air, and by any other kinds of oxidants. The oxidation process has been studied under various conditions, such as: solvent, pH, temperature, pressure, the addition of mineral salts, etc. [1-28].

Autoxidation usually means oxidation by molecular oxygen, in particular by that contained in air. The oxidation of numerous substances is autocatalysed by certain unstable and very active intermediates. In the case of hydroquinone, the oxidation to quinone passes through the intermediate semiquinone [29, 30, 31].



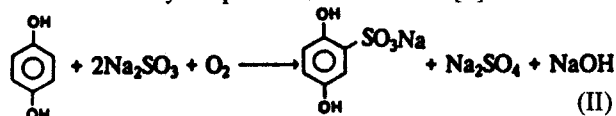
HQ $\cdot$  is not very stable, and thus acts as a reactive

**Keywords:** Hydroquinone; Autoxidation, Photographic developer

intermediate. The  $Q\cdot$  ion is a stable deep-red and can exist as a paramagnetic compound, and its stabilization is due to the resonance effect.

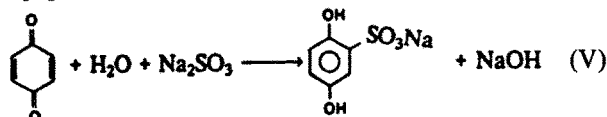
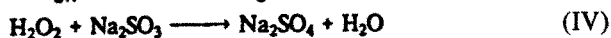
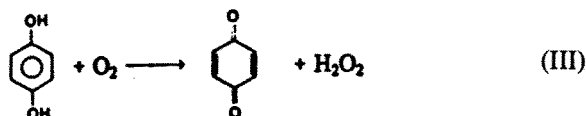
The autoxidation of the hydroquinone in alkaline solution is a complicated process. This complication is largely due to the reactivity of the hydrogen atoms attached to the benzene nucleus. In order to avoid such complications, James *et al.* [32] have studied the autoxidation of durohydroquinone (tetramethylhydroquinone). This prevents secondary reactions, which complicate the hydroquinone autoxidation. They have shown that, the autoxidation products of the hydroquinone and its homologs are corresponding quinones and hydrogen peroxide.

The oxidation of photographic developing agents by molecular oxygen have been studied by many investigators [9, 32-42]. In the presence of sulfite, the oxidation of hydroquinone is as follows [9].



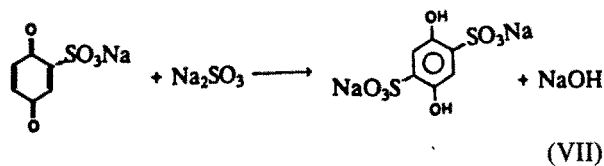
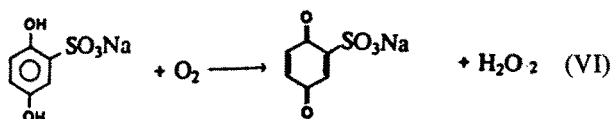
Sodium hydroquinone monosulfate has been isolated from the reaction mixture to the extent of 73% of the theoretical yield [42].

In the absence of sulfite, the first oxidation product of hydroquinone is hydrogen peroxide, and (II) appears to be composed of (III), (IV) and (V) [9].



As the oxidation proceeds, sodium hydroquinone disulfate is formed, presumably due to the oxidation of hydroquinone monosulfate and reaction of the quinone with sulfite, (VI) and (VII).

In the presence of sufficient sulfite and an alkaline solution, sodium hydroquinone monosulfate has not been detected, which means that this compound undergoes further reaction to form sodium hydroquinone disulfate.



It has also been shown [29-33] that the first step of the reaction is the formation of the doubly-charged anion ( $\text{Q}^{2-}$ ). This ion reacts with oxygen to form quinone and hydrogen peroxide.



In the pH range of 7.2-8.2, the reaction rate is proportional to the square of the hydroxyl-ion concentration. This reveals that the reaction is controlled by the concentration of the doubly charged ion [9].

A number of different methods have been used to measure the concentration of  $\text{H}_2\text{Q}$  in various solutions as well as in developers [44-58], but a

spectrophotometric method seems to be the most convenient. Since  $\text{H}_2\text{Q}$  is absorbed in the ultraviolet region, the absorbance of its aqueous solution (pH 5) at 290 nm ( $\lambda_{\text{max}}$  for  $\text{H}_2\text{Q}$ ) can be used to determine its concentration. However, the presence of metol, N-methyl-p-aminophenol (M), in the developer makes it necessary to use two wavelengths, 270 and 290 nm, in the spectrophotometric method.

Hydroquinone in a freshly prepared developer is oxidized by air and gradually loses its developing ability. No kinetic work on the oxidation of developing agent (hydroquinone) in the presence of air has been reported in the literature.

The aim of the present work was to follow the change of the concentration of hydroquinone by a spectrophotometric method and to determine the order mechanism and the half-life of the developer in the presence of air.

### Results and Discussion

The results of a typical run are given in Table 1, showing the measured absorbance in diluted solutions and the concentration of hydroquinone in the original developer in g/l.

Table 1. Results of a typical aerial oxidation at  $20.00 \pm 0.05^\circ\text{C}$  and pH 10.5

Time in hours	Absorbance <sup>a</sup>		Concentration of Hydroquinone <sup>b</sup> (g/l)	
	290 nm	270 nm	Unchanged	Consumed
0	0.504	0.260	6.20	0.00
24	0.435	0.238	5.30	0.90
46	0.393	0.205	4.77	1.43
70	0.292	0.165	3.46	2.74
95	0.200	0.132	2.23	3.90
116	0.165	0.122	1.80	4.40
130	0.095	0.060	0.93	5.27

<sup>a</sup> In diluted solution

<sup>b</sup> In the original developer solution

The percentage of the relative error in the extraction of  $\text{H}_2\text{Q}$  by ethyl acetate was found to be -0.8, which shows that almost all of the hydroquinone is extracted in the organic phase.

Using least squares method, a plot of the concentration of  $\text{H}_2\text{Q}$  as a function of time is a straight line (correlation coefficient  $r = 0.99$ , Fig. 1). This means that the aerial oxidation under the present conditions is zero-order in  $\text{H}_2\text{Q}$ , which is also in agreement with Masahiro's work [25]. If C denotes

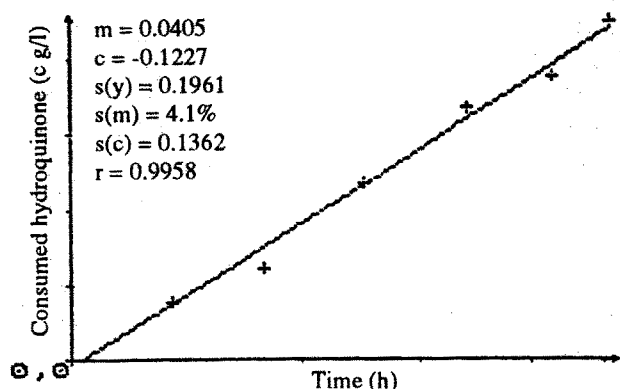


Figure 1. Plot of consumed hydroquinone (c) versus time (t) at 20°C and pH 21.5

the concentration of  $H_2Q$  in the developer, then either equation (1) or (2) can be used to correlate the experimental results. In these equations, C is in g/l and t is in hours.

$$C = 0.0405t - 0.1227 \quad (1)$$

$$\bar{R}^2 = 0.9900, SE = 0.1961, F = 594.70$$

$$C = (0.0393 \pm 8.90 \times 10^{-4})t \quad (2)$$

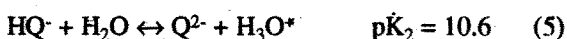
$$\bar{R}^2 = 0.9964, SE = 0.1930, F = 1945.25$$

where  $\bar{R}^2$ , SE, and F are adjusted coefficient of multiple determination, standard error, and the F-ratio for the overall significance of the regression, respectively. It seems that equation (2), which has been constrained to pass through the origin, is probably a better equation to use.

The half-life of the hydroquinone in the developer, (developer's half-life),  $t_{1/2}$ , is then given by equation (3), in which  $C_0$  is the initial concentration of hydroquinone in g/l.

$$t_{1/2} = C_0 / 0.0786 \quad (3)$$

The mechanism of the reaction can be as follows: Hydroquinone ( $H_2Q$ ) in aqueous solutions is dissociated according to equations (4) and (5)



or,



The dissociation constants are

$$K_1 = [H_3O^+][HQ^-]/[H_2Q] \quad (7)$$

$$K_2 = [H_3O^+][Q^{2-}]/[HQ^-] \quad (8)$$

$$K = K_1 \cdot K_2 \quad (9)$$

$[HQ^-]$  and  $[Q^{2-}]$  can be written in terms of  $[H_2Q]$  and dissociation constant.

$$[HQ^-] = K_1[H_2Q]/[H_3O^+] = K_1[H_2Q][OH^-]/K_w \quad (10)$$

$$[Q^{2-}] = K_1K_2[H_2Q]/[H_3O^+]^2 = K[H_2Q][OH^-]^2/K_w^2 \quad (11)$$

Since the pH of the developer solution is 10.5 and constant, the ratios of  $[HQ^-]/[H_2Q]$  and  $[Q^{2-}]/[HQ^-]$  can be easily determined.

$$\log K_1 = \log [H_3O^+] + \log [HQ^-]/[H_2Q] \quad (12)$$

or,

$$pH = pK_1 + \log [HQ^-]/[H_2Q] \quad (13)$$

$$(10.5) = 7.9 + \log [HQ^-]/[H_2Q] \quad (14)$$

Therefore

$$[HQ^-]/[H_2Q] = 407 \quad (15)$$

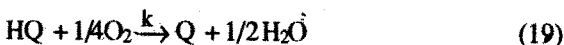
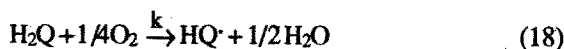
Similarly, the ratio of  $[Q^{2-}]/[HQ^-]$  is calculated from equation (8)

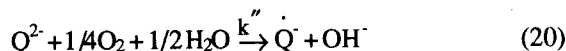
$$[Q^{2-}]/[HQ^-] = 0.81 \quad (16)$$

This shows that  $[Q^{2-}]/[H_2Q] = 320$ , and almost all of  $H_2Q$  is converted to  $HQ^-$  and  $Q^{2-}$ . Therefore, the total concentration of the  $H_2Q$  in solution is:

$$[H_2Q]_{total} = [H_2Q]_{eq} + [HQ^-]_{eq} + [Q^{2-}]_{eq} \quad (17)$$

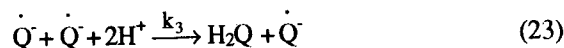
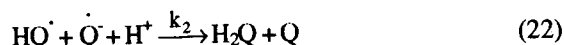
These various forms of  $H_2Q$  react with oxygen to give the intermediate radicals, semiquinones,  $HQ\cdot$  and  $Q\cdot$  [33, 43]. It should be noted that semiquinone ( $Q\cdot$ ) is a stable, deep-red compound.





where k, k' and k'' are the reaction rate constants.

It has also been shown [43] that, the HQ $\cdot$  undergoes various kinds of reactions.



where k<sub>1</sub>, k<sub>2</sub>, and k<sub>3</sub> are the reaction rate constants.

The dissociation constant of semiquinone from equation (24) is shown as:

$$K = [H^+][\dot{Q}]/[HQ\cdot] \quad (25)$$

If R denotes the total concentration of intermediate radicals, semiquinones, then,

$$R = [HQ\cdot]_{eq} + [\dot{Q}]_{eq} \quad (26)$$

[HQ $\cdot$ ] and [Q $\cdot$ ] can be given by equations (27) and (28),

$$[HQ\cdot] = R / (1 + K/[H^+]) \quad (27)$$

$$[\dot{Q}] = R(K/[H^+]) / (1 + K/[H^+]) \quad (28)$$

According to equations (21-23), the change of semiquinone concentrations as a function of time has been given as [43]:

$$-d[R]/dt = 2k_1 [HQ\cdot]^2 + 2k_2 [HQ\cdot][\dot{Q}] + 2k_3 [\dot{Q}]^2 \quad (29)$$

Substitution of equations (27) and (28) into equation (29) results in the following equation:

$$-d[R]/dt = 2R^2 [k_1 + k_2(K/[H^+]) + k_3(K/[H^+])^2] / (1 + K/[H^+])^2 \quad (30)$$

The rate of the consumed hydroquinone is also as follows:

$$-d[H_2Q]/dt = k[H_2Q] + k'[HQ^-] + k''[Q^{2-}] - k_1 [HQ\cdot]^2 - k_2 [HQ\cdot][\dot{Q}] - k_3 [\dot{Q}]^2 \quad (31)$$

Equation (31) is the sum of two equations (32) and (33),

$$d[R]/dt = k[H_2Q] + k'[HQ^-] + k''[Q^{2-}] \quad (32)$$

This is the rate of formation of radicals, semiquinones, and

$$-1/2 d[R]/dt = k_1 [HQ\cdot]^2 + k_2 [HQ\cdot][\dot{Q}] + k_3 [\dot{Q}]^2 \quad (33)$$

which is the rate of consumption of radicals, semiquinones. Now using steady-state approximation, d[R]/dt = 0, and substitution of equation (30) into equation (31):

$$-d[H_2Q]/dt = R^2 \{k_1 + k_2(K/[H^+]) + k_3(K/[H^+])^2\} / (1 + K/[H^+])^2 = R^2 \{k_1 + (k_2 \cdot K / K_w) [OH^-] + (k_3 K / K_w^2) [OH^-]^2 / 1 + (K / K_w) [OH^-]^2\} \quad (35)$$

This equation shows that:

A. The rate of reaction is zero-order with respect to hydroquinone concentration, which is in agreement with the experimental results.

B. The rate of reaction is dependent on the concentration of intermediate radicals, semiquinones, [HQ $\cdot$ ], and [Q $\cdot$ ], and according to the steady state approximation (d[R]/dt = 0), this concentration is constant. This has been confirmed by equations (15 - 17) which show that almost all H<sub>2</sub>Q changes to HQ $\cdot$  and Q<sup>2-</sup> ions, i.e., [HQ $\cdot$  + Q<sup>2-</sup>] / [H<sub>2</sub>Q] = 727. These two ions then react with oxygen to give the stable semiquinone Q $\cdot$ .

C. The rate of reaction is proportional to the square of the hydroxyl-ion concentration, which is in agreement with the results found by James *et al.* [9, 32, 33], who concluded that the reaction is controlled by the concentration of the doubly-charged ion.

D. Under atmospheric conditions the rate of reaction is independent of the concentration of oxygen.

### Experimental Section

A Perkin-Elmer UV-VIS spectrophotometer, model 550S and 1 cm fused silica absorption cells were used for all of the spectrophotometric measurements.

The composition of the standard solution used to calibrate the spectrophotometer is given in Table 2, and is exactly the same as the composition of the developer solutions used throughout this work.

**Table 2.** The composition of standard and developer solutions

Component	Sodium Sulfite	Hydroquinone	Metol	Sodium Carbonate	Potassium Bromide
C(g/l)	45	6.29	3	50	2

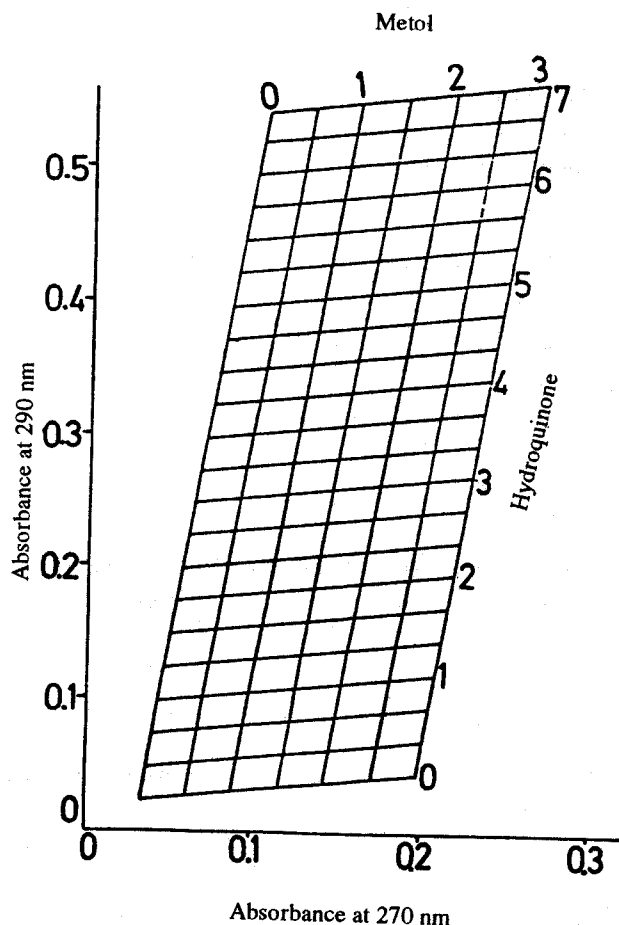
In order to establish the calibration curve, six aliquot portions of the freshly prepared standard solution (0, 10, 20, 30, 40, 50 ml) were diluted to 50 ml by distilled water. Aliquot portions (10 ml) of each diluted solution were removed and their pH were adjusted from 10.5 to 8.0, using sulfuric acid. Hydroquinone and metol of each solution was extracted with ethyl acetate (3 × 10 ml), and 1 ml portion of the organic phase diluted to 100 ml using acetate buffer of pH 5. The absorbance of each diluted solution was measured at 270 and 290 nm. Details of the calibration parameters are given in Table 3.

**Table 3.** Absorbance measurements\* for the standard solutions

Volume of Standard Solution ml	Absorbance		Concentration (g/l)	
	290 nm	270 nm	Hydroquinone	Metol
0	0.022	0.032	0	0
10	0.124	0.080	1.258	0.6
20	0.220	0.127	2.516	1.2
30	0.315	0.173	3.774	1.8
40	0.412	0.218	5.032	2.4
50	0.506	0.261	6.290	3.0

\* Average of three measurements

Since the  $\lambda_{max}$  values of hydroquinone and metol are very close, the absorbances are the sum of the absorbances of hydroquinone and metol. Therefore, the method of plotting the absorbance against concentrations of H<sub>2</sub>Q and M (Fig. 2) was the same as the one used by Rees and Anderson [53].



**Figure 2.** Calibration grid

The developer solution was prepared (Table 2), and equal volumes (50 ml) of the solution were transferred into twelve (No 1-12) 100 ml Erlenmeyer flasks protected from light with aluminium foil. The flasks were kept in a thermostated bath at 20.00 ± 0.05°C, and continuously shaken by a mechanical shaker to ensure that the solutions were saturated by air. Aliquot portion of each flask (10 ml) was removed sequentially from time to time and its pH adjusted from 10.5 to 8.0 using sulfuric acid. The remaining H<sub>2</sub>Q and M were extracted with ethyl acetate (3 × 10 ml), and 1 ml portion of the organic phase diluted to 100 ml using acetate buffer of pH 5. The absorbance of each diluted solution was measured at 270 and 290 nm, and the concentration of the remaining hydroquinone was measured by using the calibration grid (Fig. 2).

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