Kinetic and thermodynamic properties of the aerial oxidation of hydroquinone in developer solutions

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The aerial oxidation kinetics of hydroquinone in a freshly prepared developer solution at different temperatures and pHs has been studied. The activation parameters, E_a, $\Delta G^{\#}$, $\Delta S^{\#}$, $\Delta H^{\#}$ and enthalpy of formation of activated complex, $\Delta H_f^o(X^{\#})$, are determined. The large negative value of free energy of activation $\Delta G^{\#}$ proves that hydroquinone extremely tends to be oxidized by air at optimum temperature (20℃) and optimum pH (10.5) and converts to the activated complex semiquinone. It was also found that if the pH of the developer solution is increased from 9.3 to 10.5 the reaction rate will increase by a factor of 2.

Keywords   Hydroquinone, developers, aerial oxidation, 1,4-dihydroxybenzene, developing agent

Introduction

Hydroquinone, 1,4 dihydroxybenzene is one of the most well known antioxidants which is used in the manufacturing of many chemicals such as polymers and drugs. It is also the main component of the majority of black and white developers. Hydroquinone can be oxidized by air and other kinds of oxidants. This property has provided hydroquinone with the advantage of being an inhibitor to prevent many chemicals from oxidation. Therefore, it has a great economical benefit to investigate the oxidation of hydroquinone in solutions. Some groups[1-20] have investigated the oxidation of hydroquinone under different conditions such as solvent, the pressure of oxygen, inorganic salts and the applied potential, etc. In the previous work[21] we have studied the oxidation of hydroquinone in a developer solution at 20℃ and pH 10.5 and a mechanism for the oxidation process of hydroquinone was proposed. We also found that the rate of reaction is:

(a)-Zero-order with respect to hydroquinone concentration.

(b)-Dependent on the constant concentrations of intermediate radicals, semiquinones, $HQ^{\cdot}$ and $Q^{\bar{\cdot}}$.

(c)-Proportional to the square of the hydroxyl-ion concentration.

(d)-Indenpendent of the concentration of oxygen under atmospheric pressure.

No kinetic works regarding the effects of temperature and pH on the rate of aerial oxidation of hydroquinone in developers and the related thermodynamic properties have been reported in the literature. In this work, the effect of temperature on the rate of aerial oxidation of hydroquinone in a developer was investigated. The activation parameters E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq}$ were determined. The effect of pH on the rate of oxidation process is also studied at optimum temperature, 20℃, and the developer's half-lifes ($t_{1/2}$) are determined and compared.

Experimental

All chemicals were of analytical reagent grade. A Perkin Elemer UV-Vis spectrophotometer, model 550S and 1 cm fused silica absorption cells were used for all of the spectrophotometric measurements. The developer solution with desired pH was prepared (Table 1), and 50 mL of the solution were transferred into 100 mL Erlenmeyer flasks protected from light with aluminum foil. The flasks were kept in a thermostated bath at desired temperatures (± 0.05℃), and were continuously shaken by a mechanical shaker to ensure that the solutions

were saturated by air. Aliquotes of each flask (10 mL) were removed sequentially and its pH was adjusted from 10.5 to 8.0 using few drops of concentrated sulfuric acid to quench the reaction. The remaining hydroquinone (H_2Q) and metol (M) were extracted with ethyl acetate (3 × 10 mL), and 1 mL of 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 calculated by:

$$A_{270} = a_H(H_2Q) + a_M(M) \tag{1}$$

$$A_{290} = a_H(H_2Q) + a_M(M) \tag{2}$$

where A is the absorbance measured with 1 cm fused silica cells, (H_2Q) and (M) are the concentrations of hydroquinone and metol in diluted solutions, in $g \cdot L^{-1}$, and a_H and a_M are the absorptivities of hydroquinone and metol, respectively.

To calculate the concentration of hydroquinone in the presence of metol, the absorptivity of hydroquinone

and metol had to be determined. Therefore standard solutions of hydroquinone, and of metol of different concentrations (Table 2) were prepared in acetate buffer of pH 5, and the absorbance of these solutions were measured at 270 and 290 nm.

The relative indeterminate concentration error, $\delta C/C$, in spectrophotometric measurements had also to be determined[22] by:

$$\frac{\delta C}{C} = \frac{0.434}{\log T} \frac{\delta T}{T} \tag{3}$$

where $\delta T/T$ is the relative indeterminate error in transmitance, T (Table 3). It is concluded from Table 3 that the best range for the absorbance measurements is 0.2—0.7, in which the relative error is about ± 1.5%. Therefore, the absorptivity of M and H_2Q were obtained by taking the corresponding absorbances to this range.

$$A_{270} = 8.803(H_2Q) + 7.309(M) \tag{4}$$

$$A_{290} = 23.989(H_2Q) + 1.063(M) \tag{5}$$

Table 1   Composition of standard developer solutions

Component	Sodium sulfite	Hydroquinone	Metol	Sodium carbonate	Potassium bromide
C (g/L)	45	6.29	3	50	2

Table 2   Absorptivity measurement of metol (M) and hydroquinone (H_2Q) at 270 and 290 nm*

C (g/L)**	Absorbance (270 nm)	Absorbance (290 nm)	$a_{270,M}$	$a_{290,M}$	a_{270,H_2Q}	a_{290,H_2Q}
0.3010	-	0.320 (M)	7.140	1.063	-	-
0.1505	1.095 (M)	0.159 (M)	7.276	1.056	-	-
0.0602	0.440 (M)	0.065 (M)	7.309	1.080	-	-
0.02522	0.222 (H_2Q)	0.605 (H_2Q)	-	-	8.803	23.989

* All measurements were carried out at 20°C and pH 5 and a's calculated by $a = A/b.c$, $b = 1$ cm, Beer-Labert law.

** Standard solutions (Table 1) of M without H_2Q and H_2Q without M as stock solutions were prepared in acetate buffer, and diluted to desired concentrations by acetate buffer of pH 5.

Table 3   Relative error in spectrophotometric measurements (%)

T	0.800	0.700	0.600	0.500	0.400	0.368	0.300	0.200	0.100	0.030
A	0.097	0.155	0.222	0.301	0.399	0.434	0.525	0.699	1.000	1.523
$\Delta C/C$	± 2.80	± 2.00	± 1.63	± 1.44	± 1.36	± 1.34	± 1.38	± 1.55	± 2.17	± 4.75

These absorptivities were also evaluated by calibration curves. Solutions (Table 4) of different concentrations of H_2Q and M were made up in acetate buffer of pH 5 by diluting the standard solution (Table 1). The ab-

sorbance of these solutions were then measured at 270 and 290 nm. The adjusted coefficients of multiple determination, and the F-ratios for overall significance of the regression of the calibration curves (adjusted $R_2 = 1$, F

= 2819471 for 290 nm, and adjusted $R^2 = 0.9999$, F = 114353 for 270 nm) showed that the absorbance range of 0.2—0.7 is the best range to use. Therefore, the ab-

sorptivity which were obtained through this range of absorbance are the most corrected ones in this work.

Table 4 Absorbance of solutions* of H_2Q and M at 270 and 290 nm

No.	Concentration (g/L) H_2Q	Concentration (g/L) M	Absorbance (270 nm)	Absorbance (290 nm)
1	0.0210	0.0100	0.257	0.514
2	0.0189	0.0090	0.232	0.463
3	0.0168	0.0080	0.206	0.410
4	0.0147	0.0070	0.181	0.360
5	0.0126	0.0060	0.153	0.308
6	0.0105	0.0050	0.128	0.257

* To make sure that Eqs. (4) and (5) can be applied to different concentration ratio of H_2Q /M, two stock solutions, a (H_2Q 6.3, M 3.0 $g \cdot L^{-1}$) and b (H_2Q 4.618, M 3.922 $g \cdot L^{-1}$) were prepared in acetate buffer, and diluted to desired concentration by acetate buffer of pH 5. These data are correspond to solution a, and the adjusted R^2s that obtained by linear regression analysis from the solution b's data were the same.

Unknown transients are formed that interfere with the λ_{max} of the hydroquinone. To eliminate this spectral interference the unreacted hydroquinone in the developer solution had to be extracted. The relative error of the extraction process was also found to be 0.8% which shows that almost all hydroquinone is extracted by ethyl acetate and the small percentage of error arise from the impurities.

The oxidation process were studied at pH 10.5 and temperatures 20, 25, 30, 35, 40, 45, 50, 55, and 60 ℃, and also at two more different pHs 9.8 and 9.3 at the optimum developing temperature, 20 ℃. The rate constants of the reactions were then determined.

Results and discussion

The absorbance measurements of the standard solutions allow two simultaneous Eqs. (4) and (5) to be constructed for the concentration of hydroquinone (H_2Q) and metol (M) in diluted solutions of different concentration ratios of H_2Q/M for the spectrophotometric analysis.

Using least square method, a plot of the concentration of consumed H_2Q as a function of time was found to be a straight line (correlation coefficient $R = 0.99$) which is in agreement with the previous work[21] and shows that the reaction is zero order with respect to H_2Q. If the concentration of consumed H_2Q in developer is denoted

as $C_0 - C$, then either Eq. (6) or (7) can be used to correlate the experimental results.

$$C_0 - C = kt + \text{constant} \qquad (6)$$

$$C_0 - C = kt \qquad (7)$$

where C_0 and C are the initial concentration and the concentration of hyroquinone at any time in $g \cdot L^{-1}$, respectively, t is the time in hours (h), and k is the reaction rate constant in $g \cdot L^{-1} \cdot h^{-1}$. Adjusted coefficient of multiple determination, R^2, standard error, SE, and F-ratio for the overall significance of the regression, F, for all temperatures except 50, 55 and 60 ℃ (Table 5) show that Eq. (7) which has been constrained to pass through the origin (constant = 0) is a better equation to use. Results of the 9 runs are given in Table 5. It is shown that an increase of 10 ℃ in temperature will increase the rate of reaction by a factor of about 1.5.

According to the Arrehnius equation

$$\log k = \log A - \frac{E_a}{2.303 RT} \qquad (8)$$

a plot of $\ln k$ vs. $1/T$ is a straight line with the slop of $-E_a/R$ and intercept of $\ln A$. The activation energy and the preexponential factor A were then found to be 37.31 $kJ \cdot mol^{-1}$ and 1.93×10^5 $g \cdot L^{-1} \cdot h^{-1}$, respectively.

Table 5   Rate constants[a] at different temperatures and pH 10.5

Temperature (T/K)	k^b ($g \cdot L \cdot^{-1} h^{-1}$)	k^c ($g \cdot L \cdot^{-1} h^{-1}$)	Adjusted $R^{2\,d}$	F
293.15	0.04250	0.03953	0.998 (0.995)	3586 (1144)
298.15	0.05949	0.05416	0.998 (0.995)	690 (150)
303.15	0.06228	0.05490	0.994 (0.989)	1280 (657)
308.15	0.09978	0.08703	0.991 (0.979)	857 (331)
313.15	0.11469	0.10272	0.994 (0.983)	1361 (415)
318.15	0.15800	0.13701	0.993 (0.992)	1384 (1002)
323.15	0.18320	0.16152	0.994 (0.996)	1866 (2595)
328.15	0.22392	0.19897	0.995 (0.999)	2198 (9641)
333.15	0.25397	0.22372	0.994 (0.997)	1428 (3254)

[a] Average of three measurements. [b] Eq. (7). [c] Eq. (6). [d] Values in bracket correspond to Eq. (6).

The thermodynamic quantities of activation state $\Delta H^{\neq} = 37.31$ kJ·mol^{-1}, $\Delta G^{\neq} = -4.8$ kJ·mol^{-1}, and $\Delta S^{\neq} = -143.6$ J·K^{-1}·mol^{-1}, at the optimum temperature, 20°C, and optimum pH, 10.5, of developing process were also obtained by using the following equations.

$$\Delta S^{\neq} = R\ln\frac{hA}{kT} \qquad (9)$$

$$\Delta H^{\neq} \cong \Delta E_a \qquad (10)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (11)$$

where $k = 1.381 \times 10^{-23}$ J·K^{-1}, $h = 6.626 \times 10^{-34}$ J·s, and $R = 8.314$ J·K^{-1}·mol^{-1} are the Boltzmann, Planck, and gas constants, respectively. Since the enthalpy of formation of hydroquinone is known, $\Delta H_f(H_2Q) = -186.82$ kJ·mol^{-1},[23] the enthalpy of the formation of the activated complex $\Delta H_f(X^{\neq})$ can be determined.

$$\Delta H_f(X^{\neq}) = \Delta H^{\neq} + \Delta H_f(H_2Q)$$
$$= -149.29 \text{ kJ} \cdot \text{mol}^{-1} \qquad (12)$$

It has been previously[21] shown that the ratio of $\{[Q^{2-}] + [HQ^-]\}/[H_2Q] = 727$ holds, which indicates that almost all of the H_2Q is converted to HQ^- and Q^{2-}. These two ions then react with oxygen to give the stable semiquinone Q^-. The negative value of the free energy of activation confirms the short half-life and the conclusion that obtained in the previous work. It is also concluded that the developing agent extremely tends to be oxidized by air at optimum temperature and pH and converts to activated complexes semiquinones $HQ^{\cdot}$ and Q^{-}.

The aerial oxidation of developer was also studied at two more different pHs 9.3 and 9.8 at the optimum temperature of developing process 20°C. The following equations were derived to correlate the concentration of hydroquinone with time. The half-life of developer, $t_{1/2}$, in hours at 20°C can also be determined by:

$$t_{1/2} = \frac{C_0}{0.0850} = 74 \qquad (\text{pH } 10.5) \qquad (13)$$

$$t_{1/2} = \frac{C_0}{0.0519} = 122 \qquad (\text{pH } 9.8) \qquad (14)$$

$$t_{1/2} = \frac{C_0}{0.03556} = 177 \qquad (\text{pH } 9.3) \qquad (15)$$

where the denominator of these equations is equal to $2k$ (rate constant). C_0 is the initial concentration of hydroquinone in $g \cdot L^{-1}$ in the developer solutions.

It is concluded from these results that the half-life of the developer is decreased with increase of the pH of the developer solution.

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