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Kinetics and mechanism of the oxidative color removal from Durazol Blue 8 G with hydrogen peroxide

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Abstract

The kinetics of oxidation of the direct dye Durazol Blue 8G with H_2O_2 was studied spectrophotometrically in different media. An induction period was observed at the early stages of the reaction. The slowness of the oxidation reaction was a precursor of an autocatalytic behaviour. The absorbance $A = f(t)$ curve has a sigmoid character with a point of inflection which is typical of autocatalytic reactions. The kinetic and activation parameters were determined at time tending to zero ($t \rightarrow 0$) and in the bulk for uncatalyzed and autocatalyzed reactions. The reaction followed zero-order kinetics with respect to [dye] and first-order kinetics with respect to [H_2O_2]. The reaction at $t = 0$ followed a first-order kinetics for both [dye] and H_2O_2]. This means that the order as a function of the initial concentration was greater than that as function of time with respect to [dye]. This is an indication for the autocatalytic behaviour. The activation energy, E increases in the following order: phosphate buffer (pH $>$ 8) = sodium tetraborate/NaOH buffer $<$ NaOH solution $<$ phosphate buffer (pH = 8). The value of $\Delta G^{\#}$ is in the 86.2–96.3 kJ/mol range. The isokinetic relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ for the oxidation reaction in different media gives two parallel lines with a slope (isokinetic temperature) equal to 273.7 K. This temperature is lower than the average experimental temperature (313 K). This result provides evidence that the oxidation reaction of the dye with H_2O_2 in the different media follows the same mechanism and the reaction is entropy controlled. A reaction mechanism was proposed and was found to be coincident with the experimental findings.

Keywords: Direct phthalocyanine dye; Hydrogen peroxide; Autoxidation; Buffer solution; Spectrophotometery; Kinetics; Mechanism

1. Introduction

The phthalocyanines are large ring (macrocyclic) structures produced by the linking together of four phthalonitrile molecules around a central metal atom. The natural pigments termed porphyrins, such as haemoglobins and chlorophyll, have similar structures. The color of the phthalocyanines is dictated by the nature of the metal atom present. Copper phthalocyanine, first marketed by ICI in 1934 as "Monastral Fast Blue BS", is commercially of greatest importance [1]. Being insoluble, the phthalocyanines cannot be used as fabric dyes, but they are in great demand as pigments for coloring plastic, paints and printing ink. They are extremely stable and exceptionally resistant to light bleaching [1].

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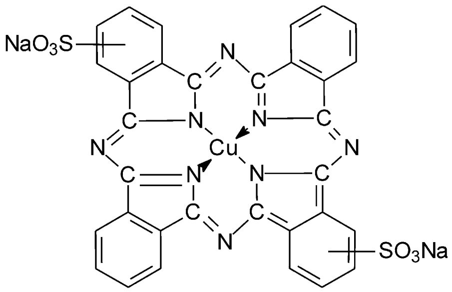
Copper phthalocyanine crystals are monoclinic with two differently oriented Cu^{2+} ions per unit cell [2]. Metal phthalocyanines are used as catalysts in many reactions. Recently, different catalyst samples of nickel (II) and copper (II) phthalocyanines supported over bentonite clay (Indian type) have been used in the polymerization of methyl methacrylate in different media [3].

Sulphonated copper phthalocyanines are soluble and are used as fabric dyes. Tetrasulphonated copper phthalocyanine is an acid dye (C.I. Acid Blue 249) and it dyes wool a very bright greenish-blue shade [4]. Disulphonate copper phthalocyanine is a direct dye (C.I. Direct Blue 86) and it is known as Durazol Blue 8G; I. It is strongly substantive towards cellulosic fibers and it possesses an extremely bright greenish-blue color with good light-fastness but poor wet-fastness [4]. This dye was chosen to be investigated in the present work as an example of direct dyes based on phthalocyanine structure. The direct dyes are inexpensive and easy to apply, and although of different wet-fastness, their use spreads with great rapidity because they fulfill an outstanding demand.

The strong coupling of the orbital of the phthalocyanine system and the central ion favour electron transfer from the metal to the π-system of the phthalocyanine ligand and vice versa. Hence, oxidation and reduction of the complex is facilitated. Bisulphite-catalyzed borohydride reduction of the dye I was studied [5].



I

Durazol Blue 8G (74180)

(ε= 13500 L mol^{-1} cm^{-1})

Critical search of literature provided little information on the chemical oxidation of the direct dye I. Thus, one of the objectives of the present work was to study the kinetics and mechanism of the chemical oxidation of this dye with H_2O_2 in different media. The matter of handling such a type of research is certainly an overwhelming contribution in order to shed some light on the chemical oxidation behavior of I, particularly for those engaged with this compound and generally for those involved in this field.

2. Experimental

2.1. Materials

Durazol Blue 8G; I (Aldrich) was used as received. Its stock solution was prepared in doubly distilled H_2O and was diluted to the desired concentrations. H_2O_2 (30% volume, stabilizing free) was obtained from Winlab (England). The exact concentration of a freshly prepared H_2O_2 solution was determined with standard $KMnO_4$ solution [6]. Other chemicals were of analytical reagent grade and were used without further purification.

2.2. Measurements

Kinetic runs were carried out under pseudo first-order conditions by keeping the H_2O_2 concentration 200-fold in excess of that of the dye. The change in absorbance of I was monitored using the conventional spectrophotometric technique. The measurements were performed in a 1-cm cell on Shimadzu 2100 S UV/vis spectrophotometer.

The cell holder temperature was held constant electronically by the aid of an attached Shimadzu temperature controller. The oxidation reaction of I with H_2O_2 does neither occur in aqueous acidic medium nor at pH below 7.0. The reaction was very slow at pH 7.0. For this reason the oxidation reaction was carried out in alkaline buffer solutions. Phosphate buffer solutions in the pH 8.0–11.55 range have been used and a few drops of NaOH solution were added to attain higher pH values [7]. Sodium tetraborate/NaOH buffer solution (pH = 10.85) as well as NaOH solutions (0.267×10^{-3}–2.0×10^{-3} M) were used, too.

3. Results and discussion

The spectrum of I in doubly distilled H_2O exhibits two bands at λ_{max} 616 and 333.5 nm. However, in phosphate buffer solutions, these bands are shifted to 607 and 328.8nm, whereas in sodium tetraborate/NaOH buffer solution the bands are shifted to 610 and 331.3 nm. In NaOH solutions no change in λ_{max} of the two bands was observed. The decay of the absorbance at λ_{max} 607, 610 and 616 nm was monitored in phosphate buffer solutions (Fig. 1), in sodium tetraborate/NaOH buffer solution and in NaOH solutions, respectively.

The absorbance, $A = f(t)$ curve of the oxidation reaction of I has a sigmoid character with a point of inflection which is typical of autocatalytic reactions (Fig. 2). The time corresponding to the point of inflection, t_{inf} was determined (Table 1). This time decreases with increasing rate constant of the autocatalyzed reaction. The extent of reaction corresponding to the point of inflection x_{inf} was determined (Table 1), and it is practically equal to half the initial dye concentration, i.e. $x_{inf} = \frac{a}{2}$[8]. The point of inflection on the reactant consumption curve evidently corresponds to the greatest reaction rate (maximum velocity, V_{max}); the slope of the tangent at this point ($-\mathrm{d}(a-x)/\mathrm{d}t$) has a maximal value at this moment. In this connection the passage of the rate through a maximum at $x = \frac{a}{2}$ is generally characteristic of autocatalytic reactions [8,9]. From Fig. 2 it is clear that the reaction proceeds with an induction period during which the product-catalyst accumulates [10]. The induction period may have an influence on the value of t_{inf} . This is clear in Table 1 where the values of t_{inf} (30–45 °C) with sodium tetraborate/NaOH buffer solution (pH = 10.85) are greater than those with phosphate buffer solution

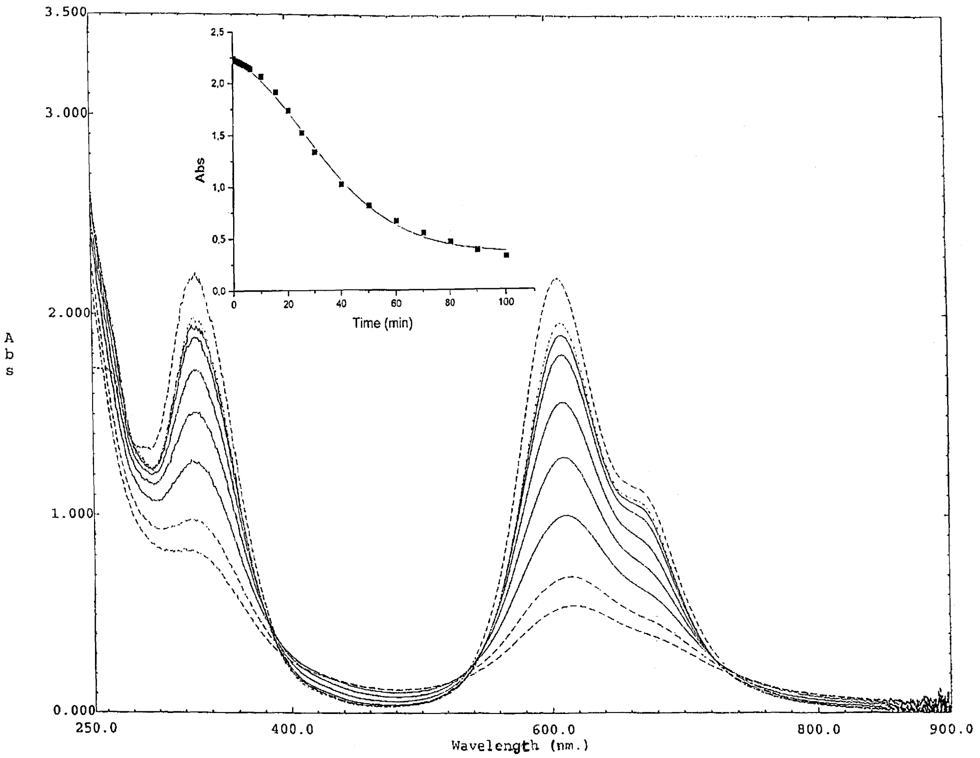


Fig. 1. Time sequence of the decrease in the absorbance band at $\lambda_{max} = 607$ nm for the oxidation of Durazol Blue 8G (1.67×10^{-5} M) with 0.033 M H_2O_2 in phosphate buffer solution (pH = 8.0) at 30 °C.

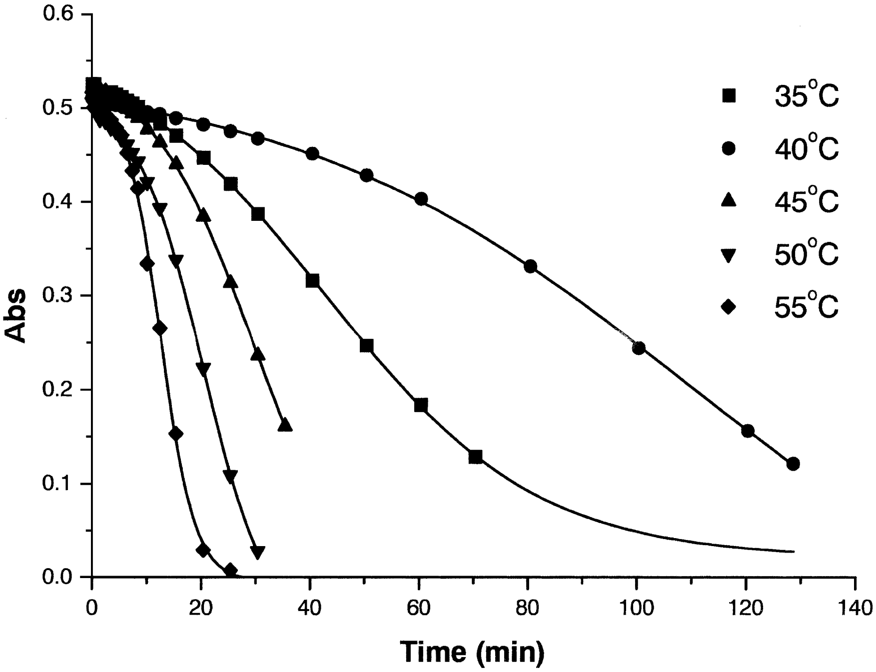


Fig. 2. Typical illustration of the relationship between absorbance and time for the oxidation reaction of Durazol Blue 8G (3.33×10^{-5} M) with H_2O_2 (0.12 M) in phosphate buffer (pH = 8.0) at different temperatures.

(pH = 9.57), although the values of the rate constant of the autocatalytic reaction, k_c with the former are greater than those with the latter.

Also, with NaOH solution $\left(2.0 \times 10^{-3}\ \mathrm{M}\right)$ at 35 °C the value of t_{inf} is greater than that with phosphate buffer (pH = 9.57) at the same temperature, although the value of k_c with the former is greater than that with the latter. This means that the induction period with sodium tetraborate/NaOH buffer solution (30–45 °C) as well as with NaOH solution $\left(2.0 \times 10^{-3}\ \mathrm{M}\right)$ at 35 °C is more pronounced than that with phosphate buffer solution (pH = 9.57) at the same temperatures (Fig. 3 and Table 1). This means that a low rate of the reaction in its initial period, followed by rapid growth of the product yield in the successive period due to the increase in the amount of the catalyst have been observed. Thus, each curve has been analyzed into two linear parts representing the slow uncatalyzed reaction and the fast autocatlyzed one. The pseudo zero order kinetic equation;

$$A = A_o - k_o t \tag{1}$$

has been applied to both linear parts, where A_o is the initial absorbance of the substrate (dye) at zero time, A the absorbance of the substrate at time t and k_o is the observed rate constant. This means that the order with respect to the dye concentration is equal to zero, and

$$k_o = k[H_2O_2] \tag{2}$$

where k is the specific rate constant. In the case of the autocatalyzed reaction Eq. (2) becomes

$${}_ok_c = k_c[H_2O_2] \tag{3}$$

where ${}_ok_c$ and k_c are the observed and the specific rate constants, respectively. Fig. 4 is a graphical representation of Eqs. (2) and (3) and it provides evidence that the order with respect to $[H_2O_2]$ is unity. Hence, the values of k and k_c at a given temperature can be directly determined from Eqs. (2) and (3), respectively. Moreover, the initial rate, V_0 and the order as a function of the initial con-

Table 1
Kinetic parameters of the oxidation of Durazol Blue 8G with H_2O_2 in various media, at $t \rightarrow 0$, and for uncatalyzed and autocatalyzed reactions

Medium	pH	t °C	$k'_o\times10^3$ l mol^{-1} s^{-1}	$V_o\times10^9$ M s^{-1}	$k_o\times10^4$ M s^{-1}	$K\times10^3$ s^{-1}	${}_ok_c\times10^4$ M s^{-1}	$k_c\times10^3$ s^{-1}	$x_{inf}\times10^5$ M	t_{inf} min	$V_{max}\times10^6$ M s^{-1}
Phosphate buffer	8.0	35	0.60	2.39	0.33	0.28	0.75	0.62	1.51	109.35	0.046
		40	0.90	3.61	0.73	0.61	1.11	0.93	1.18	42.69	0.069
		45	1.79	7.16	1.03	0.86	2.41	2.01	1.88	29.25	0.149
		50	2.97	11.86	1.70	1.42	3.87	3.22	1.70	20.24	0.239
		55	4.89	19.54	2.80	2.33	6.45	5.37	1.91	12.60	0.398
Phosphate buffer + 6%(w/w) *t*-butanol	8.0	40	0.54	2.15	0.40	0.34	0.79	0.66	1.62	99.43	0.049
		45	1.14	4.57	0.77	0.64	1.68	1.40	1.54	61.40	0.104
		50	1.49	5.95	1.27	1.06	2.28	1.90	1.32	39.27	0.141
		55	2.60	10.39	2.10	1.75	3.26	2.71	1.21	21.88	0.201
Phosphate buffer	9.57	30	1.40	7.70	1.40	4.20	5.37	16.30	5.71	27.16	1.207
		35	2.15	11.80	1.98	6.00	8.13	24.60	5.43	16.18	1.822
		40	3.27	18.0	3.53	10.71	12.27	37.20	6.16	14.30	2.756
		45	4.90	27.0	5.20	15.76	19.10	57.90	6.13	8.760	4.289
Sodium tetraborate/NaOH buffer	10.85	30	1.72	9.51	1.45	4.38	7.80	23.60	6.92	58.21	1.748
		35	2.59	14.25	2.03	6.16	11.57	35.00	6.87	37.57	2.593
		40	3.92	21.60	3.26	9.88	17.33	52.50	6.78	23.91	3.889
		45	6.40	35.05	4.72	14.30	24.17	73.00	6.70	16.17	5.407
		50	7.65	42.14	6.24	19.00	34.67	105.00	6.33	11.55	7.778
2×10^{-3} M NaOH solution		35	4.05	22.30	3.48	10.60	12.50	37.90	5.60	20.14	2.807
		40	8.34	46.00	5.81	17.60	25.20	76.10	6.90	10.09	5.637
		45	12.62	69.50	11.1	33.60	51.30	156.0	7.20	6.840	11.556
		50	20.80	114.7	13.14	39.80	63.20	191.50	7.30	5.370	14.185

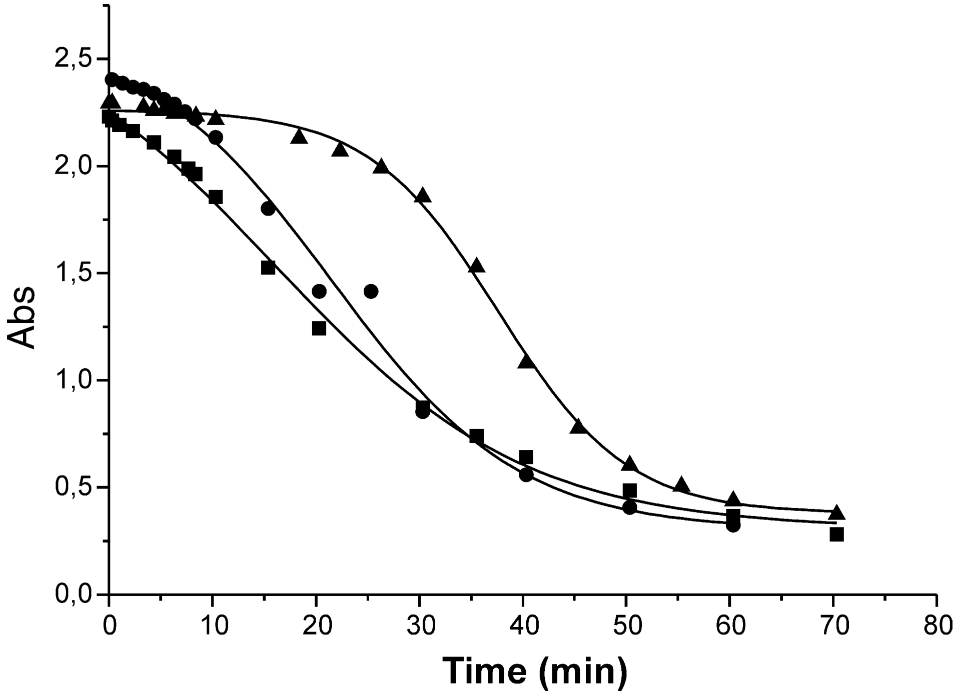


Fig. 3. Typical illustration of the relationship between absorbance and time for the oxidation reaction of Durazol Blue 8G (1.67 × 10^{-4} M) with H_2O_2 (0.033 M) in different media at 35 °C. ■: Phosphate buffer solution (pH = 9.57); •: NaOH solution (2× 10^{-3}M); ▲: sodium tetraborate/NaOH buffer solution (pH = 10.85).

centration with respect to H_2O_2 and the dye at time tending to zero ($t \to 0$) were also determined. This was done by determining the initial absorbance change $(dA/dt)_o$ from the intercept of (dA/dt) vs. absorbance curves [7]. The order at $t \to 0$ was the same with respect to [dye] and $[H_2O_2]$ and was found to be equal to unity (Figs. 5 and 6). This means that the order as a function of the initial concentration of the dye was greater than that as a function of time (zero-order). This is an indication of the autocatalytic behaviour [9]. Thus, the rate equation at $t \to 0$ can be written down as follows

$$V_o = k'_o[\text{dye}][H_2O_2] \qquad (4)$$

where k'_o is the initial rate constant at $t \to 0$. The values of k'_o and V_o for the oxidation reaction at $t \to 0$; k_o and k for the uncatalyzed reaction; ${}_ok_c$, k_c, x_{inf}, t_{inf}, and V_{max} for the autocatalyzed oxidation reaction are collected in Table 1. It is clear that the value of V_{max} is always greater than that of V_o. The values of the rate constants and those of V_o and V_{max} increased with increasing the pH of the medium in the following sequence: phosphate buffer (pH = 8.0) < phosphate buffer (pH = 9.57) < sodium tetraborate/NaOH buffer (pH = 10.85). With NaOH solution (2× 10^{-3} M) all kinetic parameters were the greatest.

The effect of pH on the rate constant was studied using constant concentrations of all participants at 45 °C. The pH was varied from 8 to 11.55 using phosphate buffer solutions. The rate constants, k'_o, k_o and ${}_ok_c$ of the reaction at $t \to 0$, uncatalyzed reaction and autocatalyzed reaction, respectively, were plotted vs. pH (Fig. 7). Generally, the reaction rate increases with increasing pH until reaching a maximum at pH = 10.85 and then decreases with increasing pH. This may be due to the repulsion between the perhydroxyl ions (HO_2^-) and the SO_3^- groups of the dye at higher pH values. This electrostatic repulsion renders the reaction between the dye molecule and HO_2^- less facile. The effect of NaOH concentration on the

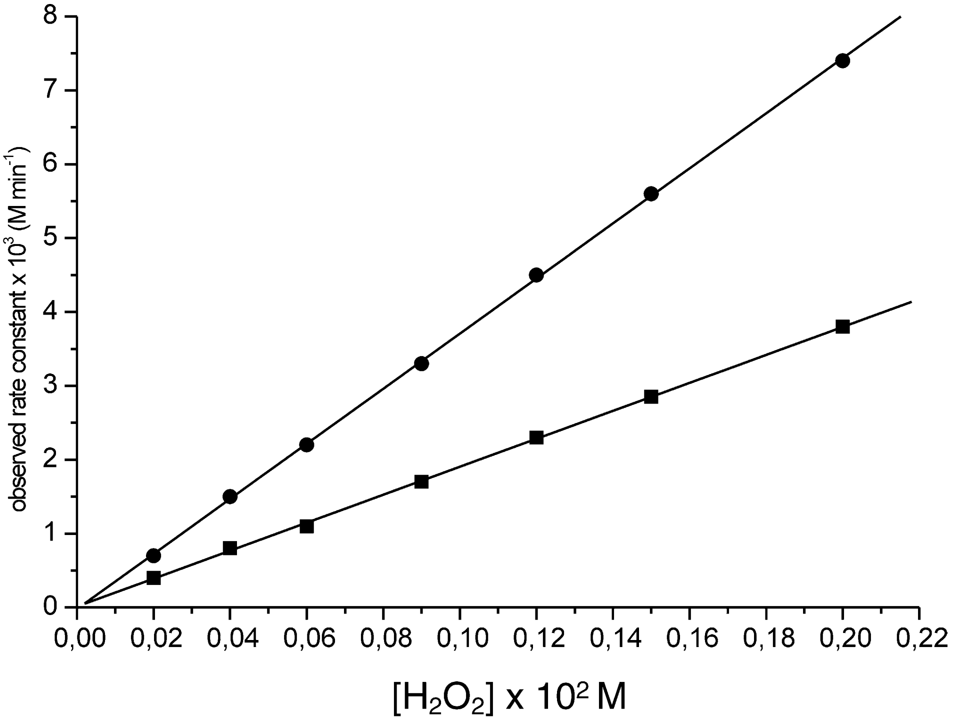


Fig. 4. A plot of the observed rate constant vs. [H_2O_2] for the oxidation reaction of Durazol Blue 8G (6.67×10^{-5}M) in phosphate buffer solution (pH = 8.0) at 35 °C: ■: uncatalyzed reactions; •: autocatalyzed reaction.

observed rate constant, $_{o}k_{c}$ of the autocatalyzed oxidation reaction of I was investigated at 50 °C (Fig. 8). The value of $_{o}k_{c}$ increases with increasing NaOH concentration and it reaches a maximum at a NaOH concentration of 1.33×10^{-3}M, then it decreases with increase of the latter. This shows the same phenomenon that was observed in Fig. 7. Moreover, the plot of $_{o}k_{c}$ vs [NaOH] (Fig. 8), starts from the zero point. This means that in the absence of NaOH, there exists no autocatalytic behaviour during the oxidation reaction of I. This is clearly observed in Fig. 9 which illustrates the $A = f(t)$ plot of the oxidation of I with H_2O_2 at pH 7.0. On the other hand, when k_o of the uncatalyzed reaction and V_o at $t \rightarrow 0$ were plotted vs. [NaOH], a linear relationship with non-zero intercept was obtained (Figs. 10 and 11). The value of the intercept in Fig. 10 corresponds to the value of k_o (1.25×10^{-4} M s^{-1}) of the uncatalyzed reaction at pH 7 at 50 °C. The value of the intercept in Fig. 11 corresponds to the value of V_o at $t \rightarrow 0$ (1.0×10^{-8} M s^{-1}) at pH 7 at 50 °C. This means that the reaction can be carried out in neutral medium (pH = 7.0) but it is very slow and shows no autocatalytic behaviour.

The formation of free radicals during the autocatalytic oxidation process was confirmed using 6% (w/w) *t*-butanol in phosphate buffer (pH = 8.0) at various temperatures (Table 1). In the presence of this scavenger the rate of the reaction decreased obviously.

The activation energy, E was determined by applying Arrhenius equation. The change in the free energy of activation, $\Delta G^{\neq}$ was evaluated from Eyring's equation [8]

$$k = \frac{k_b T}{h} e^{-\Delta G^{\#}/RT} \qquad (5)$$

where k_b is the Boltzmann's constant and h is the Planck's constant.

The change in the enthalpy of activation $\Delta H^{\#}$ was deduced from the relationship [8]

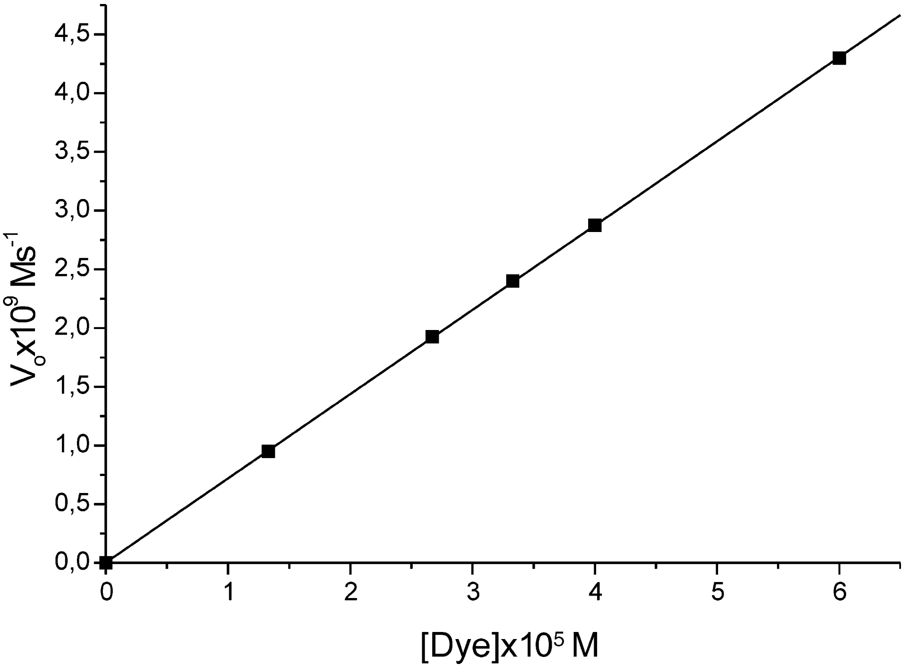


Fig. 5. A plot of the initial rate V_o at $t \to 0$ and [dye] for the oxidation reaction of Durazol Blue 8G with H_2O_2 (0.12 M) in phosphate buffer (pH = 8.0) at 35 °C.

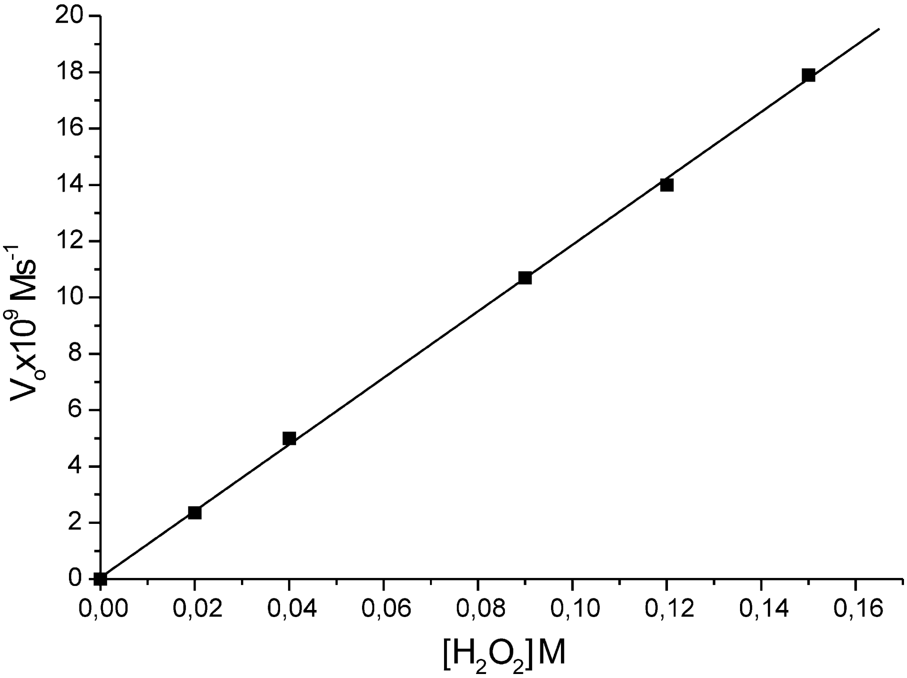


Fig. 6. A plot of the initial rate V_o at $t \to 0$ and $[H_2O_2]$ for the oxidation of Durazol Blue 8G (6.67 × 10^{-5} M) in phosphate buffer solution (pH = 8.0) at 45 °C.

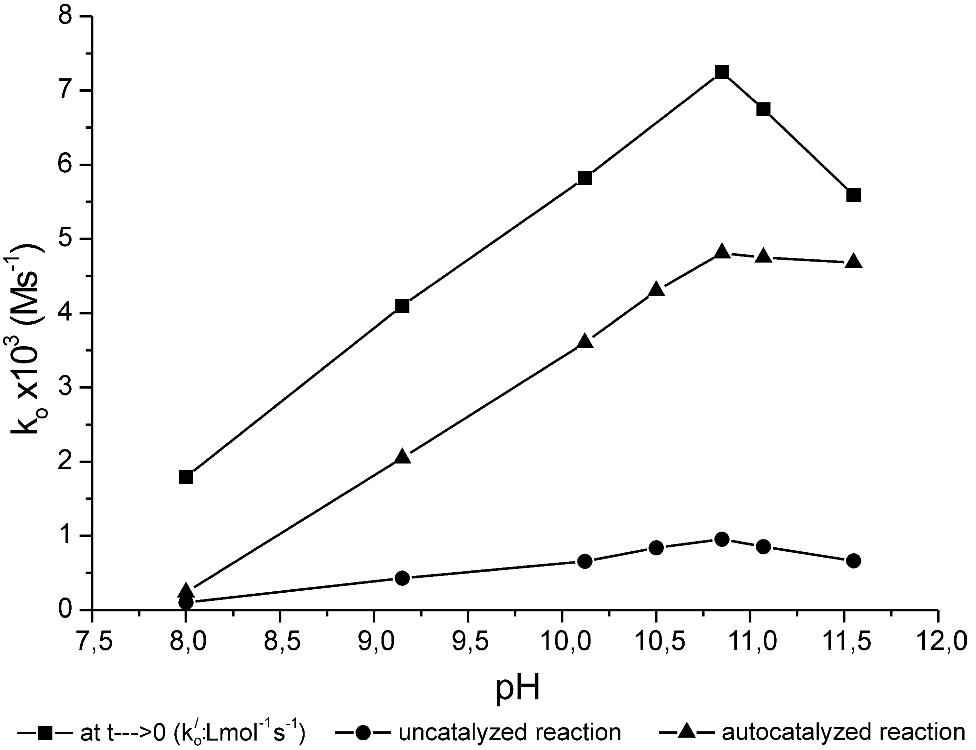


Fig 7. A plot of the observed rate constant k_o vs. pH (phosphate buffer) for the oxidation reaction of Durazol Blue 8G (1.67×10^{-4} M) with H_2O_2 (0.033 M) at 45 °C.

$$\Delta H^{\#} = E - RT \tag{6}$$

The change in the entropy of activation was determined from the relationship [8]

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{7}$$

All activation parameters are collected in Table 2. The values of E and $\Delta S^{\neq}$ increase in the following order: sodium tetraborate/ NaOH buffer <phosphate buffer (pH>8.0)<NaOH solution <phosphate buffer (pH=8.0). The greater the value of $\Delta S^{\neq}$ the greater is the probability of the activated complex formation. The value of $\Delta G^{\neq}$ is in the 86.2-96.3 kJ/mol range.

The isokinetic relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ of the autocatalytic oxidation of I with H_2O_2 in different media gives two parallel straight lines whose slope β (isokinetic temperature) is equal to 273.7 K, Fig. 12. This result provides evidence that the oxidation reaction of I by H_2O_2 in different media follows one mechanism, i.e. the same rate determining step (r.d.s). The fact that the points for the catalyzed reaction appear to fall on the same line (although in different regions) as the points for the uncatalyzed reaction, suggests an essential identity of mechanism for the two reactions [11]. Additionally, the oxidation reaction of I is entropy-controlled [11]. It is interesting to note that one of the two parallel lines (upper line) in Fig. 12 is related to the phosphate buffer solution (pH=8.0) in the absence and in the presence of *t*-butanol. The other line (lower line) is related to all other media that contain NaOH, i.e. phosphate buffer (pH > 8.0), sodium tetraborate/NaOH buffer and NaOH solution. Solvent changes often alter the enthalpy and entropy of activation of a reaction. If the solvents in a series perform closely similar roles in the reaction, it is expected, and often found, that the enthalpy of activation is a linear function of the entropy of the activation [11]. In some reactions solvents fall into two qualitatively different classes and the activation

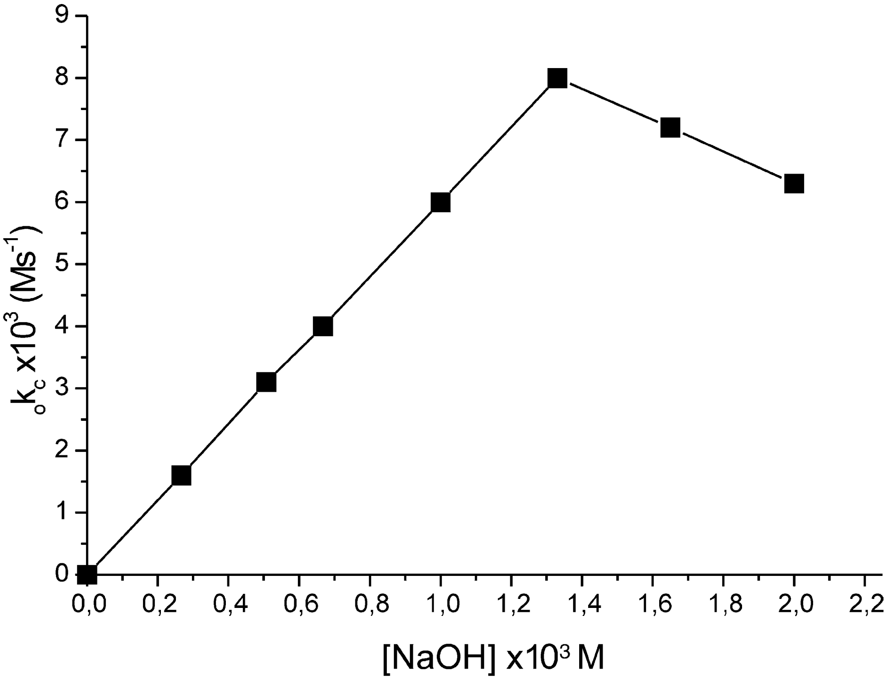


Fig. 8. A plot of the observed rate constant vs. [NaOH] for the autocatalytic oxidation reaction of Durazol Blue 8G (1.67×10^{-4} M) with 0.033 M H_2O_2 at 50 °C.

Table 2
Activation parameters of the oxidation of Durazol Blue 8G with H_2O_2 in different media at $t \to 0$, and for uncatalyzed and autocatalyzed reactions

Medium	pH	Activation parameters (kJ/mol)[a]	$t \to 0$	Uncatalyzed reaction	Autocatalyzed reaction
Phosphate buffer	8.0	E	93.8	90.6	93.4
		$\Delta H^{\#}$	91.2	88.0	90.8
		$\Delta G^{\#}$	96.3	96.3	95.9
		$\Delta S^{\#}$	−16.2	−26.3	−16.0
Phosphate buffer + 6%(w/w) *t*-butanol	8.0	E	92.9	93.1	91.5
		$\Delta H^{\#}$	90.2	90.4	88.8
		$\Delta G^{\#}$	96.5	96.2	96.0
		$\Delta S^{\#}$	−19.7	−18.1	−22.5
Phosphate buffer	9.57	E	66.9	64.0	64.1
		$\Delta H^{\#}$	64.3	61.4	61.5
		$\Delta G^{\#}$	86.0	86.2	85.1
		$\Delta S^{\#}$	−70.0	−80.0	−76.0
Sodium tetraborate/NaOH	10.85	E	66.4	64.7	63.6
		$\Delta H^{\#}$	63.8	62.1	61.0
		$\Delta G^{\#}$	86.2	88.1	86.5
		$\Delta S^{\#}$	−71.6	−83.1	−81.5
NaOH solution (2×10^{-3} M)		E	82.7	80.6	78.6
		$\Delta H^{\#}$	80.1	78.0	76.0
		$\Delta G^{\#}$	83.8	85.8	84.5
		$\Delta S^{\#}$	−11.7	−24.7	−26.9

[a] $\Delta S^{\#}$: J mol^{-1} deg^{-1}.

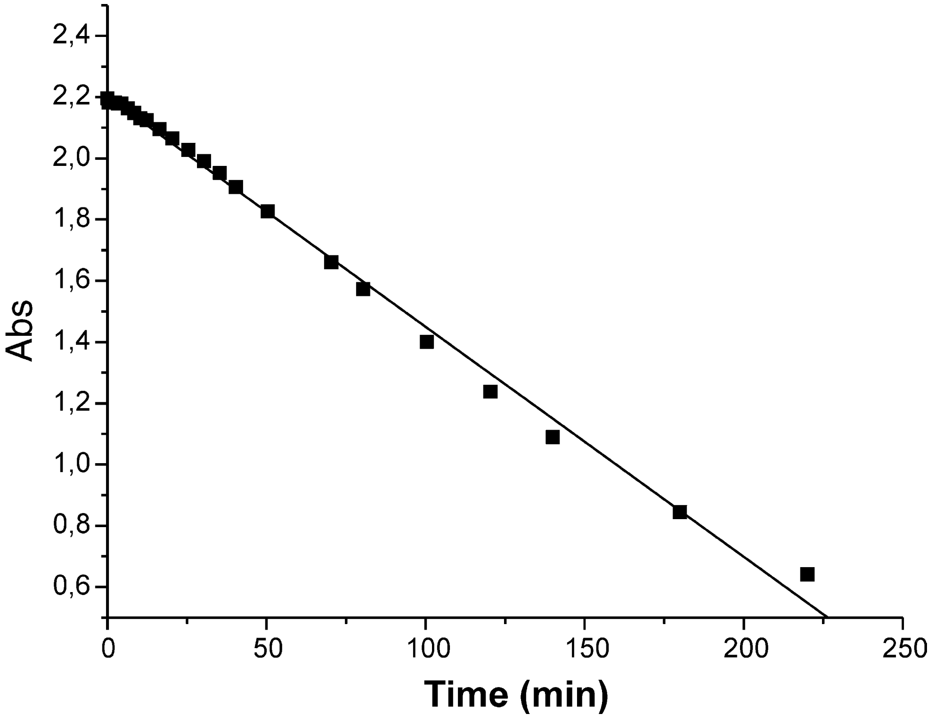


Fig. 9. Absorbance–time relationship of the oxidation reaction of Durazol Blue 8G (1.67 × 10^{-4} M) with 0.033 M H_2O_2 in phosphate buffer (pH = 7.0) at 50 °C.

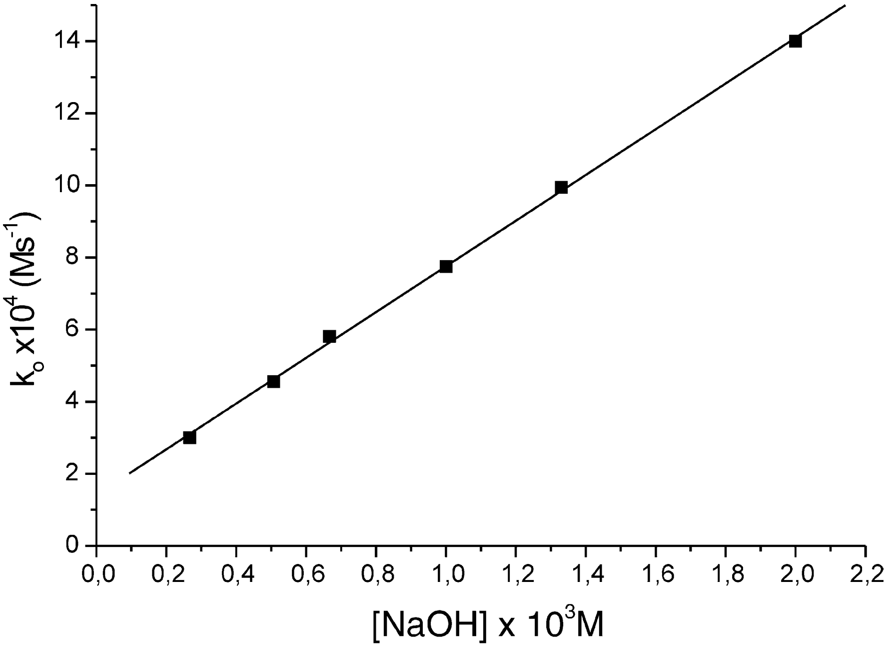


Fig. 10. A plot of the observed rate constant vs. [NaOH] for the uncatalyzed oxidation reaction of Durazol Blue 8G (1.67 × 10^{-4} M) with 0.033 M H_2O_2 at 50 °C.

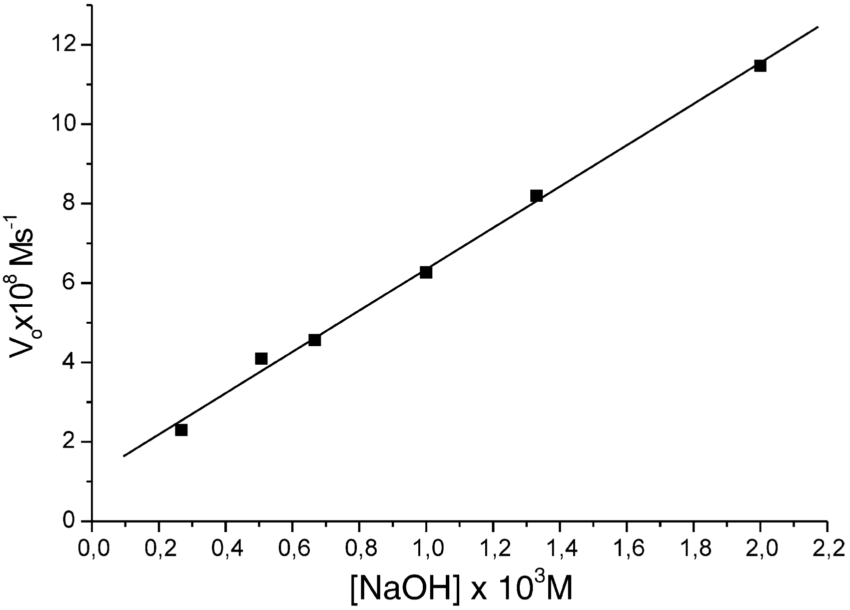


Fig. 11. A plot of the initial rate V_o at $t \rightarrow 0$ vs. [NaOH] for the oxidation reaction of Durazol Blue 8G (1.67×10^{-4} M) with 0.033 M H_2O_2 at 50 °C.

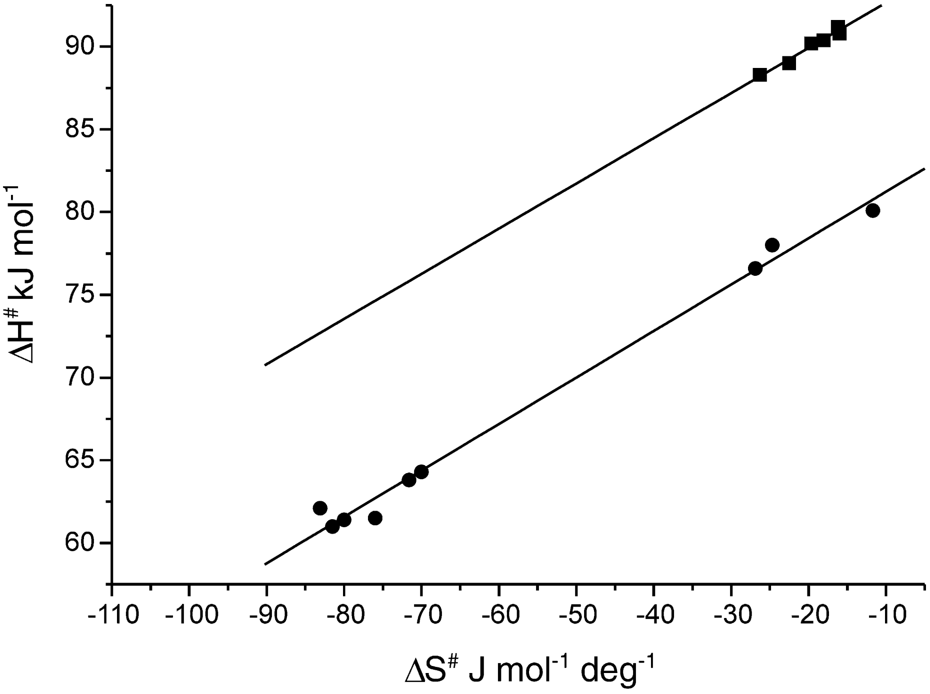


Fig. 12. Illustration of the isokinetic relationship by plotting $\Delta H^{\#}$ vs. $\Delta S^{\#}$ for the oxidation reaction of Durazol Blue 8G (3.33×10^{-5}–1.67×10^{-4} M) with H_2O_2 (0.033–0.12 M) in different media: ■: phosphate buffer (pH = 8.0) in absence and presence of *t*-butanol; •: phosphate buffer (pH = 9.57), sodium tetraborate/NaOH buffer (pH = 10.85) and NaOH solution (2×10^{-3} M).

parameters in the isokinetic relationship fall on two lines rather than on a single one. An example is the decomposition of triethylsulfonium bromide in hydroxylic solvents and in non-hydroxylic solvents, where the activation parameters ($\Delta H^{\#}$ and $\Delta S^{\#}$) fall on two parallel lines. One of the two lines is related to the reaction in hydroxylic solvents and the other line is related to the reaction in non-hydroxylic solvents. The explanation for this discontinuous solvent effect may be due to a double potential energy minimum that either the ground or transition state may have [11].

According to the above experimental observations and explanations, the following mechanism is proposed taking into consideration that the dye molecule I contains Cu^{2+}, and it would be represented by I^{2+} to consider the ionic charges in both sides of each chemical equation.

$$H_2O_2 \xrightarrow{k_1} HO_2^- + H^+ \tag{8}$$

$$I^{2+} + HO_2^- \xrightarrow{k_2} I(HO_2)^+ \tag{9}$$

$$I(HO_2)^+ + I^{2+} \xrightarrow[\text{slow}]{k_3} I_2\left(H\dot{O}_2\right)^{3+} \tag{10}$$

$$\begin{aligned} I_2\left(H\dot{O}_2\right)^{3+} + H_2O_2 &\xrightarrow[\text{fast}]{k_4} I^{2+}\dot{O} \\ &+ I\left(\dot{O}H\right)^+ + 1/2O_2 + H_2O \end{aligned} \tag{11}$$

$$I\left(\dot{O}H\right)^+ + H_2O_2 \xrightarrow{k_5} I^{2+}\dot{O} + OH^- + H_2O \tag{12}$$

$$H^+ + OH^- \rightarrow H_2O \tag{13}$$

$$I^{2+}\dot{O} + I^{2+}\dot{O} \rightarrow I_2^{4+}O_2 \tag{14}$$

The rate equation can be written down in terms of the slow step, i.e. the r.d.s [Eq. (10)] as follows:

$$V = k_3\left[I(HO_2)^+\right]\left[I^{2+}\right] \tag{15}$$

Applying the steady-state approximation principle for HO_2^- and I $(HO_2)^+$, then the rate Eq. (15) becomes:

$$V = k_1[H_2O_2] \tag{16}$$

This is in good agreement with the experimental findings that the reaction follows first-order kinetics with respect to $[H_2O_2]$ and a zero-order kinetics with respect to the [dye]. The r.d.s in this mechanism is the reaction between $I(HO_2)^+$ and a dye molecule I which contains Cu^{2+} ion $\left(I^{2+}\right)$. The product of the r.d.s. is the active intermediate that contains a univalent cuprous ion in one of the two dye molecules. In many systems, Cu^{I}–Cu^{II} oxidation-reduction cycle is involved [12,13]. The active intermediate reacts with the original reactant (H_2O_2) to form the final products. This step requires relatively low activation energy, particularly when the active species is free radical and is therefore very fast [14]. In contrast, the formation of the active intermediate from the stable original molecule does require high activation energy and cannot be fast. In order for the reaction over active intermediates to proceed rapidly, it is necessary that these intermediates be regenerated in the course of the reaction. In other words, it is necessary that the reaction between the intermediate and the original reactant yields not only the stable product but also two or several molecules of active intermediates. This renders the kinetics of autocatalysis and branched chain reactions to be closely related [8]. Chain termination is the process in which the active intermediate is irrevocably annihilated [Eq. (14)] [14,15].

When the percentage of *t*-butanol increased from 6 to 8% in the reaction medium in phosphate buffer solution of pH 8.0 at 45 °C, neither the observed rate constant ${}_{o}k_c$ of the autocatalyzed reaction $\left(1.68 \times 10^{-4}\ M\ s^{-1}\right)$ nor the value of V_{max} $\left(0.104 \times 10^{-6}\ M\ s^{-1}\right)$ has been changed. This is because the concentration of the catalyst product (free radical active intermediate) has reached a nearly time-invariant value after the occurrence of the induction period at the early stage of the autoxidation process [15].

4. Conclusion

The oxidation reaction of the direct dye Durazol Blue 8G with H_2O_2 is very slow in neutral medium and does not occur in acidic medium. This is because in acidic medium, no perhydroxyl ions (HO_2^-) are set free and the oxidation process does not take place. In alkaline medium the hydroxyl ions neutralize the hydrogen ions, thereby promoting the liberation of the active perhydroxyl ions. The oxidation of the dye I is characterized by an autocatalytic behavior. The reaction was found to be entropy controlled. After the oxidation of the dye I, its blue color disappears.

The natural cotton, which is bleached with H_2O_2, should be thoroughly rinsed before being treated with the dye I. The dyeing process takes place in alkaline medium ($pH > 9$) at a high temperature. So, any traces of H_2O_2 on the bleached cotton may cause the oxidation of the dye leading to a patchy cloth and inhomogeneous dyeing process.

Even more interesting is that the present work provides the optimum conditions to employ the oxidizing properties of H_2O_2 in alkaline medium as a tool for color removal of the direct dye Durazol Blue 8G in the wastewater stream in dyeing and textile fabrics. The optimum conditions are working at $pH = 10.85$ and in 1.33×10^{-3} M NaOH solution.

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