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Kinetics and mechanism of the uncatalyzed and Ag(I)-catalyzed oxidative decolorization of Sunset Yellow and Ponceau 4R with peroxydisulphate

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Abstract

The kinetics and mechanism of the oxidation of Sunset Yellow (E-110, C.I. 15985), SY, and Ponceau 4R (E-124, C.I. 16255), PR, monoazo dyes with peroxydisulphate have been investigated. The oxidation reaction of SY and PR was very slow and followed a zero-order kinetics for [dye] and a first-order kinetics for $[S_2O_8^{2-}]$. The reaction showed an activation energy of 102.3 kJ/mol and 96.2 kJ/mol for SY and PR, respectively. The rate of the Ag(I)-catalyzed oxidation reaction was higher with an activation energy of 46 kJ/mol and 45 kJ/mol for SY and PR, respectively. The activation parameters, $\Delta H^{\#}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ were also deduced. A reaction mechanism was proposed for the oxidation reaction of SY and PR in the absence and in the presence of Ag(I).

Keywords: Sunset Yellow; Ponceau 4R; Peroxydisulphate; Catalysis; Kinetics

1. Introduction

Sunset Yellow (E-110) (formula **I**, SY) and Ponceau 4R (E-124) (formula **II**, PR) are synthetic monoazo dyes Scheme 1. They are used as colorants in common foods and drugs [1].

Determination of SY and PR in various media has been investigated [2,3]. Many factors can contribute to the instability of colorants. Trace metals, for example, zinc, tin, aluminum, iron and copper are known to cause fading of some additives. Azo dyes in particular are troublesome in this regard in that they often react with food cans and at a rate proportional to their concentration. This may cause corrosion of the container and a corresponding loss in the food dye content [1,4]. The decolorization reactions of dyes and colorants are very important in some ecological aspects, for example, waste treatment of dyeing and food fabrics.

Critical search of literature provided little information on the chemical oxidation and decolorization of the two concerned dyes. Thus, one of the objectives of the present work was to study the kinetics and mechanism of the oxidative decolorization reaction of SY and PR with $S_2O_8^{2-}$. The matter of handling such type of research is certainly an overwhelming contribution in order to shed some light on the chemical oxidation behaviour of these dyes, particularly for those engaged with these compounds and generally for those involved in this field.

2. Experimental

2.1. Materials

Sunset Yellow (E-110) and Ponceau 4R (E-124) are Aldrich products. They were used as received. Their stock solutions were prepared in double distilled H_2O and were diluted to the desired concentrations. $K_2S_2O_8$ (Merck) was recrystallized from double distilled H_2O. Its solution was immediately prepared before the measurements to avoid the change of

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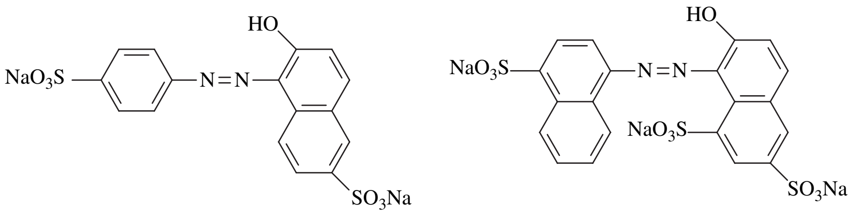


Sunset Yellow, SY
(E-110, C. I. 15985)
I

Ponceau- 4R, PR
(E-124, C. I. 16255)
II

Scheme 1.

concentration due to self-decomposition. Other chemicals were of analytical reagent grade and were used without further purification. The reaction temperature was in the range of 35–50 ± 0.1 °C.

2.2. Kinetic measurements

Kinetic runs were carried out under pseudo-first-order conditions in solutions containing excess $S_2O_8^{2-}$. The change in absorbance of **I** ($\lambda_{max} = 483$ nm) and **II** ($\lambda_{max} = 507$ nm) was monitored spectrophotometrically using a UV/vis 2100S Shimadzu recording spectrophotometer, Fig. 1. It is equipped with a thermoelectrically temperature controlled cell holder (TCC-260) at high accuracy over a temperature range of 7–60 °C. All reactions were conducted in a 1 cm spectrophotometer cell.

3. Results and discussion

Although the kinetics runs were measured under pseudo-first order conditions, the reaction organized a new adaptation mechanism and the pseudo-zero-order kinetics with respect to the dye concentration imposed itself on the oxidation reaction. The observed rate constant, k_o, was determined from zero-order kinetics plot, $A = A_o - k_o t$, as shown in Fig. 2, where A is the absorbance at time t, A_o is the absorbance at $t = 0$. The k_o value was determined for both SY and PR at different temperatures. For the determination of the order with respect to $[S_2O_8^{2-}]$ Ostwald's method was applied where the observed rate constant, k_o is plotted vs. $[S_2O_8^{2-}]$ [5]. A straight line from the zero point was obtained whose slope is equal to the specific rate constant, k, as shown in Fig. 3. This means that the order with respect to $[S_2O_8^{2-}]$ with both dyes was equal to unity. Fig. 3 follows the following equation:

$$k_o = k\left[S_2O_8^{2-}\right] \tag{1}$$

The value of k at a given temperature can be deduced directly from Eq. (1). Thus, the rate equation for the oxidation of SY and PR can be written down as follows:

$$V = k\left[S_2O_8^{2-}\right] \tag{2}$$

The activation energy, E, can be evaluated by introducing the values of k into an Arrhenius plot. The change in the enthalpy of activation, $\Delta H^{\#}$ is calculated from the following relationship [6,7]:

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

The change in the free energy of activation, $\Delta G^{\neq}$ is determined from Eyring's equation [6,7].

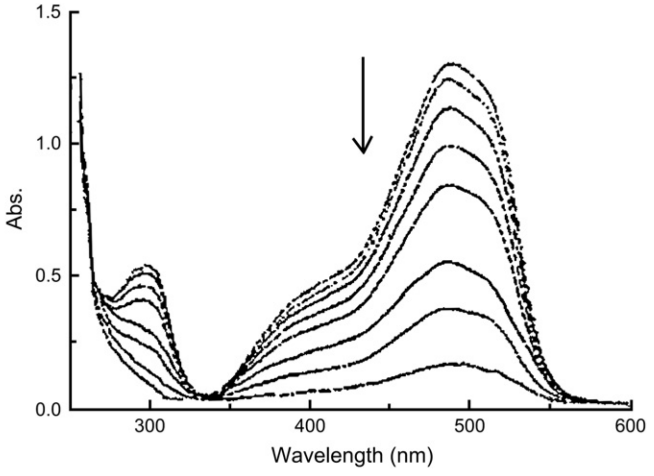


Fig. 1. Time sequence of the decrease in the absorption band at $\lambda_{max} = 483$ nm for the reaction of Sunset Yellow (6.67×10^{-5} M) with peroxydisulphate (0.067 M) at 50 °C.

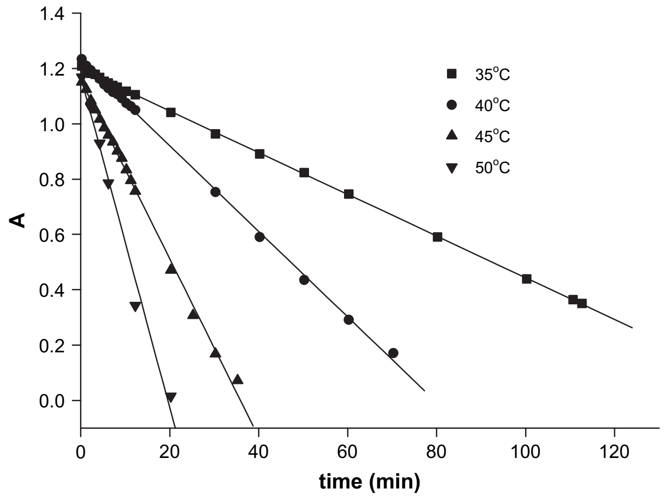


Fig. 2. Oxidation of Sunset Yellow (6.67×10^{-5} M) with peroxydisulphate (0.06 M) in the absence of Ag(I) at different temperatures.

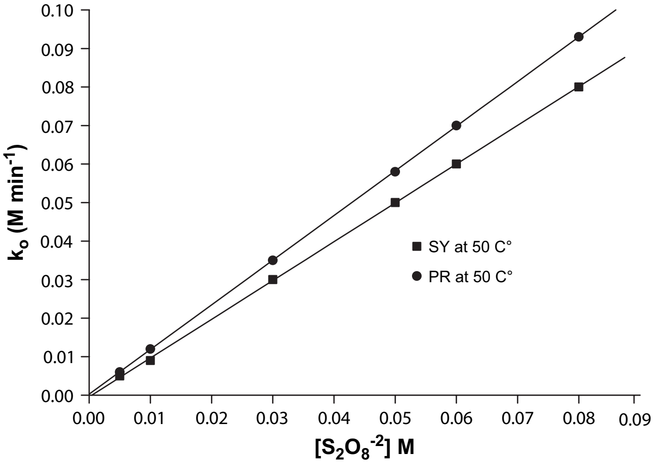


Fig. 3. Effect of peroxydisulphate concentration on the observed rate constant of the oxidation reaction of Sunset Yellow (6.67×10^{-5} M) at 50 °C and Ponceau 4R (2.65×10^{-5} M) at 50 °C.

$$k = \frac{KT}{h} e^{-\Delta G^{\neq}/RT}$$

The change in the entropy of activation, $\Delta S^{\neq}$ is calculated from the following relationship [6,7]:

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

The values of k_o, k and the activation parameters for the uncatalyzed oxidation of SY and PR with $S_2O_8^{2-}$ in aqueous medium are summarised in Table 1.

As a free radical scavenger *t*-butanol was used to investigate the existence of free radicals that are involved in the reaction mechanism. *t*-Butanol (18% w/w) was used with SY and PR. The value of k_o decreased in the presence of *t*-butanol, indicating the existence of free radicals during the oxidation reaction (Table 1).

The influence of the ionic strength on the rate of the oxidation reaction of SY and PR was examined in a $NaNO_3$ medium. The influence was evaluated by applying Brønsted–Bjerrum equation [6–8],

$$\log k = \log k' + 2AZ_AZ_B\sqrt{\mu}\left(1 + \sqrt{\mu}\right) \qquad (3)$$

where, μ is the ionic strength of the reaction medium and, is given by $\mu = 1/2\sum c_i z_i^2$. The sum is made for all the ions present in the reaction medium, k and k' are the specific rate constants in the bulk of the reaction and at infinite dilution, respectively, Z_A and Z_B are the charges of the reacting species and A is a constant that equals to 0.509×2.303 for water at 25 °C. When $\log k$ was plotted vs. $\sqrt{\mu}(1 + \sqrt{\mu})$ for the two dyes a straight line was obtained whose slope (Z_A, Z_B) was equal to zero, as shown in Fig. 4. This means that the ionic strength of the medium has no effect on the specific rate constant. This provides evidence that the oxidation reaction occurs between a neutral dye molecule and a charged ionic species.

The uncatalyzed oxidation of SY and PR with $S_2O_8^{2-}$ is associated with high values of E and $\Delta S^{\neq}$ (Table 1). The high values of these parameters suggest that the reaction is initiated by O–O bond cleavage on $S_2O_8^{2-}$ giving rise to the active $SO_4^{\bullet-}$ radical [9,10] rather than a bimolecular interaction between the substrate molecule and the oxidant ion. This latter process always shows lower values for E and $\Delta S^{\neq}$ [10,11].

Table 1
Kinetic and activation parameters for the oxidation of **I** (6.67×10^{-5} M), **II** (2.65×10^{-5}) with $S_2O_8^{2-}$ (0.05 M) in the presence and absence of Ag(I)

Colorant	t (°C)	$k_o \times 10^4$ M s^{-1}	$k \times 10^3$ s^{-1}	k_c (L mol^{-1} s^{-1})	E (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol deg)
I	35	1.29	1.92		102.3	99.7	90.4	29.5
	40	2.59	3.87					
	45	4.87	7.27					
	50	7.83	11.80					
	50 (in the presence of *t*-butanol)	2.73	5.46					
II	35	1.70	2.53		96.2	93.6	90.7	9.2
	40	2.92	5.14					
	45	6.09	9.09					
	50	10.50	14.30					
	50 (in the presence of *t*-butanol)	3.27	6.54					
I + 1.33×10^{-4} M Ag(I)	35	11.2		7.43	46.0	43.4	70.9	−87.2
	40	16.5		10.40				
	45	22.5		13.26				
	50	33.0		17.30				
II + 5.0×10^{-5} M Ag(I)	35	5.2		6.94	45.0	42.4	70.6	−89.4
	40	8.0		10.12				
	45	10.5		13.15				
	50	16.3		16.60				

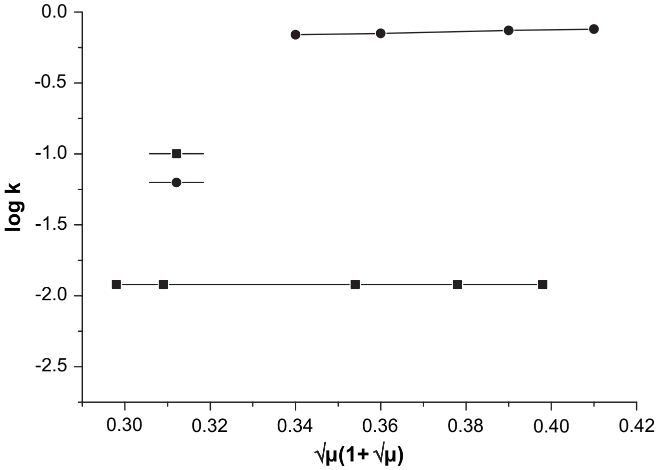
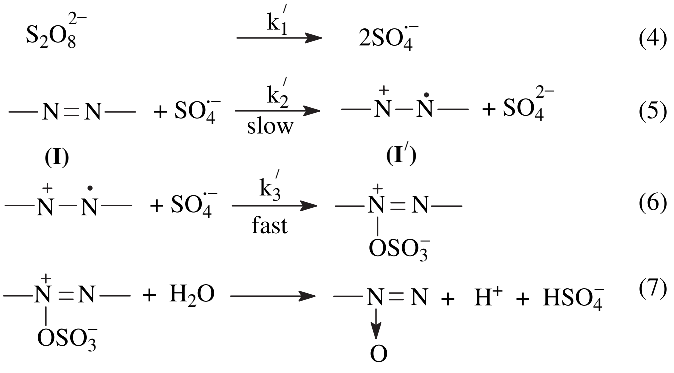


Fig. 4. Effect of ionic strength on the rate constant of the oxidation reaction of Sunset Yellow (6.67×10^{-5} M) and Ponceau 4R (3.33×10^{-5} M) with peroxydisulphate (0.05 M) at 50 °C.

The following mechanism is proposed for the uncatalyzed oxidation process of SY and PR (Scheme 2).



$$S_2O_8^{2-} \xrightarrow{k_1'} 2SO_4^{\bullet-} \qquad (4)$$

$$\underset{\textbf{(I)}}{-N{=}N-} + SO_4^{\bullet-} \xrightarrow[\text{slow}]{k_2'} \underset{\textbf{(I}'\textbf{)}}{-\overset{+}{N}-\overset{\bullet}{N}-} + SO_4^{2-} \qquad (5)$$

$$-\overset{+}{N}-\overset{\bullet}{N}- + SO_4^{\bullet-} \xrightarrow[\text{fast}]{k_3'} -\underset{OSO_3^-}{\overset{+}{N}}{=}N- \qquad (6)$$

$$-\underset{OSO_3^-}{\overset{+}{N}}{=}N- + H_2O \longrightarrow -N{=}\underset{\underset{O}{\downarrow}}{N} + H^+ + HSO_4^- \qquad (7)$$

Scheme 2.

Thus,

$$V = k_2'[-N{=}N-][SO_4^{\bullet-}] \qquad (8)$$

Applying the steady-state approximation principle for $SO_4^{\bullet 2-}$, the mechanism gives the rate law

$$V = \frac{-d[-N{=}N-]}{dt} = k_1'[S_2O_8^{2-}] \qquad (9)$$

which is consistent with the experimental rate law given in Eq. (2). The formation of the azoxy product in Eq. (7), Scheme 2 has been previously reported for the oxidation of azo-containing compounds, e.g. 4-(phenylazo)diphenylamine and some direct dyes [12,13]. $-N{=}N-$ (I) and $-N^{+}-N^{\bullet}-$ (I′) are referred to as the azo centre of the compounds **I** and **II** and their radical intermediate species, respectively. The oxidation reaction of SY and PR was very slow in the absence of a catalyst. Ag(I) was chosen to be used as a catalytic species to accelerate the reaction rate as shown in Fig. 5. A plot of the observed rate constant of the catalyzed reaction, k_o vs. [Ag(I)] is linear with non-zero intercept as shown in Figs. 6 and 7. The plot obeys Eq. (10),

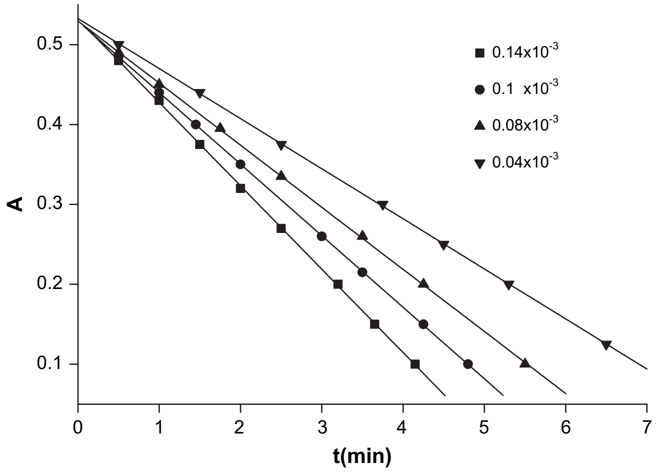


Fig. 5. Zero-order plot of the catalyzed oxidation reaction of Ponceau 4R (2.65×10^{-5} M) with peroxydisulphate (0.067 M) in the presence of different concentrations of Ag(I) at 50 °C. ▼: 0.04×10^{-3} M; ▲:0.08×10^{-3} M; ●: 0.10×10^{-3} M; ■: 0.14×10^{-3} M.

$$k_o = \text{Intercept} + k_c[\text{Ag(I)}] \qquad (10)$$

and shows that the overall reaction proceeds via the catalyzed and the uncatalyzed pathways simultaneously as was found elsewhere [14]. The order with respect to [Ag(I)] was determined by plotting $\ln k_o$ vs. ln[Ag(I)] and was found to be equal to 0.89 which can be taken as unity. The ordinate intercept in Eq. (10) represents the observed rate constant of the uncatalyzed reaction, and its value was in good agreement with that determined in the absence of Ag(I) with both dyes. k_c is the second-order rate constant of the catalyzed path and its value is determined from the slope of the linear relationship of Eq. (10). Table 1 contains the values of k_o, k_c and the activation parameters of the Ag(I)-catalyzed oxidation reaction of SY and PR. The values of $\Delta G^{\neq}$ are smaller than those of the uncatalyzed processes. This is because the greater the rate constant of the reaction, the smaller is the value of $\Delta G^{\neq}$.

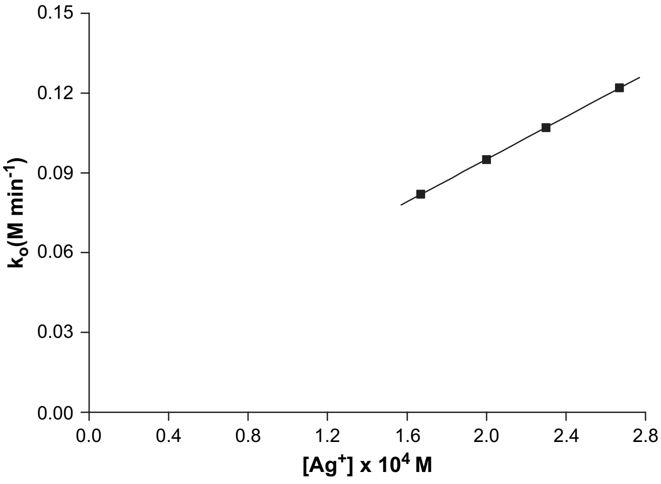


Fig. 6. Effect of Ag(I) concentration on the observed rate constant of the catalyzed oxidation reaction of Sunset Yellow (6.67×10^{-5} M) with peroxydisulphate (0.02 M) at 40 °C.

Moreover, the value of E of the catalyzed reaction was about half its value for the uncatalyzed one. The positive value of $\Delta S^{\neq}$ for the uncatalyzed oxidation reaction of SY and PR is also observed in the uncatalyzed oxidation reaction of tartrazine with $S_2O_8^{2-}$ ($\Delta S^{\neq} = 150\ \mathrm{J\,mol^{-1}\,deg^{-1}}$) whereas a negative value of $\Delta S^{\neq}$ ($-10\ \mathrm{J\,mol^{-1}\,deg^{-1}}$) was found for the Ag(I)-catalyzed process of the latter [15]. The positive value of $\Delta S^{\neq}$ is an indication of the high solvation as well as of the high probability of the formation of the activated complex. From Table 1 it is clear that the oxidation reaction of both the dyes is enthalpy controlled.

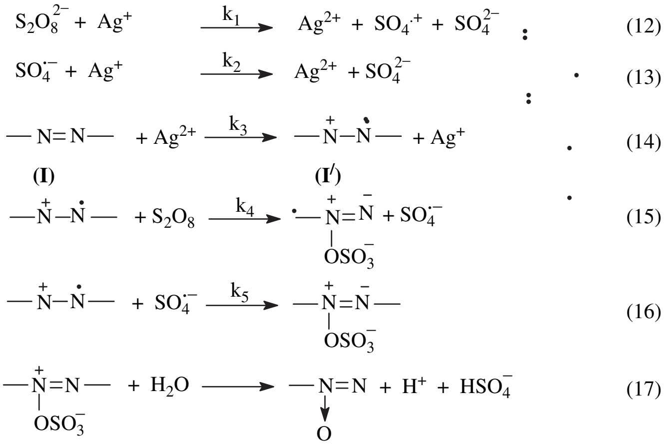
The dependence of k_o on pH for SY and PR was investigated in the presence of Ag(I) in phosphate buffer solution as shown in Fig. 8. In the case of SY the value of k_o increases as the pH rises with a break at pH = 6.0. In the case of PR the value of k_o rises to a maximum at pH = 7.0 and then decreases Fig. 8. From Fig. 7, it is clear that the pK values of SY and PR are equal to 6 and 7, respectively. These values are in good agreement with those found elsewhere [16].

In the presence of Ag(I) the reaction rate was enhanced tremendously. The reaction showed first-order dependence on the concentration of both the oxidant and the catalyst, while zero-order on that of the substrate. Besides, the results indicate that the rate equation of the catalyzed oxidation reaction can be written down as follows:

$$V = k\left[S_2O_8^{2-}\right] + k_c\left[S_2O_8^{2-}\right]\left[\mathrm{Ag(I)}\right] \tag{11}$$

The first term in Eq. (11), $k[S_2O_8^{2-}]$ is devoted to the uncatalyzed oxidation process, whereas the second term is devoted to the catalyzed one.

Thus, the following mechanism for the Ag(I)-catalyzed oxidation reaction of SY and PR can be proposed (Scheme 3).



$$S_2O_8^{2-} + Ag^+ \xrightarrow{k_1} Ag^{2+} + SO_4^{\cdot+} + SO_4^{2-} \tag{12}$$

$$SO_4^{\bullet-} + Ag^+ \xrightarrow{k_2} Ag^{2+} + SO_4^{2-} \tag{13}$$

$$\underset{\mathbf{(I)}}{-N{=}N-} + Ag^{2+} \xrightarrow{k_3} \underset{\mathbf{(I')}}{-\overset{+}{N}-\overset{\bullet}{N}-} + Ag^+ \tag{14}$$

$$-\overset{+}{N}-\overset{\bullet}{N}- + S_2O_8 \xrightarrow{k_4} {}^{\bullet}-\underset{\substack{|\\ OSO_3^-}}{\overset{+}{N}}{=}\overset{-}{N} + SO_4^{\bullet-} \tag{15}$$

$$-\overset{+}{N}-\overset{\bullet}{N}- + SO_4^{\bullet-} \xrightarrow{k_5} -\underset{\substack{|\\ OSO_3^-}}{\overset{+}{N}}{=}\overset{-}{N}- \tag{16}$$

$$-\underset{\substack{|\\ OSO_3^-}}{\overset{+}{N}}{=}N- + H_2O \longrightarrow -\underset{\substack{\downarrow\\ O}}{N}{=}N + H^+ + HSO_4^- \tag{17}$$

Scheme 3.

Application of the steady-state principle for Ag^{2+}, $SO_4^{\bullet-}$, and $-\overset{+}{N}-\overset{\bullet}{N}-$ gives

$$\mathrm{d}\left[Ag^{2+}\right]/\mathrm{d}t = k_1\left[Ag^+\right]\left[S_2O_8^{2-}\right] + k_2\left[Ag^+\right][SO_4^{\bullet-}] - k_3\left[Ag^{2+}\right][I] = 0$$

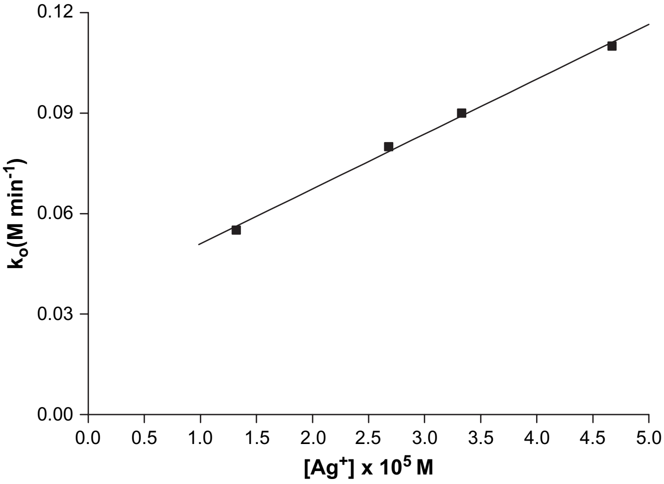


Fig. 7. Effect of Ag(I) concentration on the observed rate constant of the catalyzed oxidation reaction of Ponceau 4R (2.65×10^{-5} M) with peroxydisulphate (0.067 M) at 50 °C.

$$[I] = \frac{k_1\left[Ag^+\right]\left[S_2O_8^{2-}\right] + k_2\left[Ag^+\right][SO_4^{\bullet-}]}{k_3\left[Ag^{2+}\right]} \tag{18}$$

$$\mathrm{d}[SO_4^{\bullet-}]/\mathrm{d}t = k_1\left[Ag^+\right]\left[S_2O_8^{2-}\right] - k_2\left[Ag^+\right][SO_4^{\bullet-}] + k_4\left[S_2O_8^{2-}\right][I'] - k_5[SO_4^{\bullet-}][I'] = 0$$

$$[I'] = \frac{k_1\left[Ag^+\right]\left[S_2O_8^{2-}\right] - k_2\left[Ag^+\right][SO_4^{\bullet-}]}{k_5[SO_4^{\bullet-}] - k_4\left[S_2O_8^{2-}\right]} \tag{19}$$

$$\mathrm{d}[I']/\mathrm{d}t = k_3\left[Ag^{2+}\right][I] - k_4\left[S_2O_8^{2-}\right][I'] - k_5[SO_4^{\bullet-}][I'] = 0$$

$$[I] = \frac{k_4\left[S_2O_8^{2-}\right][I'] + k_5[SO_4^{\bullet-}][I']}{k_3\left[Ag^{2+}\right]} \tag{20}$$

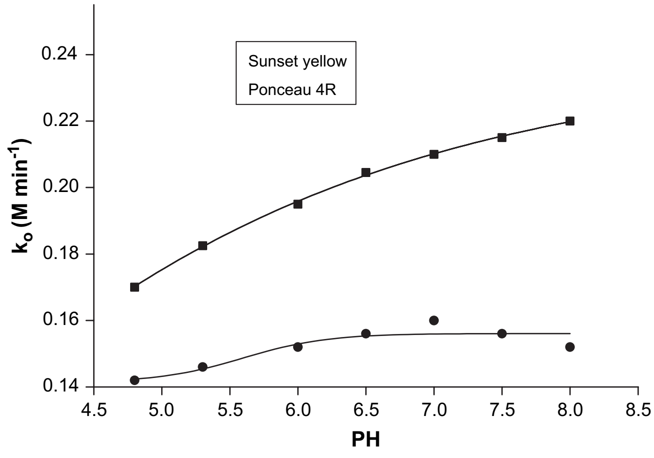


Fig. 8. Effect of pH on the observed rate constant of Ag(I)-catalyzed oxidation reaction of Sunset Yellow (6.67×10^{-5} M) and Ponceau 4R (2.65×10^{-5} M) with peroxydisulphate (0.067 M) at 45 °C.

Eqs. (18) and (20) lead to

$$k_1\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_8^{2-}}\right] + k_2\left[\mathrm{Ag^+}\right]\left[\mathrm{SO_4^{\bullet-}}\right] = k_4\left[\mathrm{S_2O_8^{2-}}\right]\left[\mathrm{I'}\right] + k_5\left[\mathrm{SO_4^{\bullet-}}\right]\left[\mathrm{I'}\right] \quad (21)$$

On substitution for [I′], Eq. (19), in Eq. (21) and further rearrangements, we have

$$k_2k_5\left[\mathrm{SO_4^{\bullet-}}\right] = k_1k_4\left[\mathrm{S_2O_8^{2-}}\right]^2$$

$$\left[\mathrm{SO_4^{\bullet-}}\right] = \left[\mathrm{S_2O_8^{2-}}\right]\left(\frac{k_1k_4}{k_2k_5}\right)^{1/2} \quad (22)$$

Combining Eqs. (18) and (22) would lead to Eq. (23).

$$[\mathrm{I}] = \frac{k_1\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_8^{2-}}\right] + k_2\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_8^{2-}}\right](k_1k_4/k_2k_5)^{1/2}}{k_3\left[\mathrm{Ag^{2+}}\right]} \quad (23)$$

$$\mathrm{Rate} = k_3\left[\mathrm{Ag^{2+}}\right][\mathrm{I}] \quad (24)$$

Eqs. (23) and (24) give the following reaction rate equation

$$\mathrm{Rate} = \left\{k_1 + \left[\frac{k_1k_2k_4}{k_5}\right]\right\}\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_8^{2-}}\right] \quad (25)$$

Eq. (25) is consistent with the Ag(I)-catalyzed pathway of the oxidation reaction as shown in Eq. (11) and confirms that the catalyzed reaction rate is dependent on the first power of both $\mathrm{Ag^+}$ and $\mathrm{S_2O_8^{2-}}$ concentrations.

This mechanism (Scheme 3) is also supported with that reported about the kinetics of Ag(I)-catalyzed oxidation of other aromatic azo compounds by peroxydisulphate [12,15], where the azoxy structure has been characterized by IR and MS [17].

When Eq. (9) is added to Eq. (25), the overall rate equation for the Ag(I)-catalyzed oxidation reaction of SY and PR can be written down as follows:

$$V = k'\left[\mathrm{S_2O_8^{2-}}\right] + \left\{k_1 + \left(\frac{k_1k_2k_4}{k_5}\right)^{1/2}\right\}\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_8^{2-}}\right] \quad (26)$$

This equation is consistent with that found for the Fe(III)-catalyzed oxidation of tartrazine with peroxydisulphate [15].

It is clear that the value of k_c in Eq. (11) is equal to $\{k_1 + (k_1k_2k_4/k_5)^{1/2}\}$ in Eq. (26).

4. Conclusions

Decolorization of the two colorants occurs during the oxidation process. This has great impact on the environmental waste treatment of the food and drug fabrics which use both the dyes. The environment in which the colorants SY and PR exist may be considered as the precursor for their oxidation and decolorization. Thus, the way of preservation of foods and drugs that are treated with both the colorants should be handled carefully. In connection with the difficulty in oxidation of SY and PR even with strong oxidizing reagent (e.g. $\mathrm{S_2O_8^{2-}}$) the present work throws light on the possibility of using them as food and drug colorants in the absence of undesired ions that render their oxidation more facile.

Acknowledgement

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