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Kinetics and mechanism of the reduction of some azo-dyes by inorganic oxysulfur compounds

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Abstract

The kinetics of the reduction of Sunset Yellow (E-110, C.I. 15985), SY, and Ponceau-4R (E-124, C.I. 16255), PR, dyes by dithinoite and bisulfite was studied using stopped-flow and conventional UV/vis spectrophotometer under *pseudo-* first order conditions. The reaction followed a total one and half-order kinetics, first order with respect to dye and half-order with respect to dithionite, while with bisulfite overall second-order kinetics has been revealed. The reduction using dithionite has higher rate constant than bisulfite. With dithionite, PR has higher rate constant compared with SY, while the reverse has been observed with bisulfite. The direct involvement of $SO_2^{\cdot-}$ radical in the reduction mechanism has been established. The formation of carbon-4 sulfonate adducts was concluded in the case of using bisulfite. Addition of β-cyclodextrin showed an enhancement in the reduction rate of SY, while no detectable effect was noticed with PR. This increase in the rate constant is attributed to the inclusion of *p*-sulfophenylazo side of SY into β-cyclodextrine cavity. Addition of cationic surfactant, CTAB, retarded the rate for both dyes due to the squeezed of dye molecules in the micellar core. The reaction was found to be an enthalpy controlled. Finally the reduction mechanism was proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dithionite; Bisulfite; Sunset Yellow; Ponceau-4R; Stopped-flow; Kinetics; Mechanism; β-Cyclodextrin

1. Introduction

The most commonly used synthetic food colors are those which possess the azo chromophor. Sunset Yellow (SY) and Ponceau-4R (PR) are synthetic azo-dyes, which are very important ingredients in many convenience foods as confectionery products, gelatin, desserts, snacks and beverages, since many of these would be colorless without the inclusion of dyes. The potential use of these dyes as food color additives has been restrained by their sensitivity to nucleophilic addition leading to their decolorization [1]. This could be occurring in the presence of sulfur dioxide or bisulfite as these are being widely used as preservatives in food industries [2–4]. Sodium bisulfite is often added to soft drinks as a preservative along with synthetic color and has been thought to participate in dye degradation. Dithionite and bisulfite are also widely used as reductants in industry. It finds use as bleaching agents in the textile, wool and paper industries, in dyeing of cellulose fiber [5], in household decolorants, in the manufacturing of various chemicals, and as a biochemical reductant [6]. Dithionite has also been used extensively in

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many chemical reactions [7–11]. The reduction by dithionite is very interesting because of its ability to reduce directly as $S_2O_4^{2-}$ or via the dissociate radical anion ($SO_2^{\cdot -}$). The presence of $SO_2^{\cdot -}$ in aqueous solution is well known [12,13] and both $SO_2^{\cdot -}$ and $S_2O_4^{2-}$ have been proven to be the reducing species of many organic compounds and inorganic complexes [14–18] as well as biological redox systems [19–22]. $SO_2^{\cdot -}$ is a stronger reducing agent than $S_2O_4^{2-}$ and is the predominant reducing species at low concentrations of dithionite, whereas at high concentrations of dithionite reduction by $S_2O_4^{2-}$ is more predominant [8].

A literature survey reveals that the kinetics of the reduction of SY and PR dyes using dithionite and bisulfite has not been investigated yet. The present study introduces an exhaustive investigation into the reduction kinetics of SY and PR dyes. In addition, the effects of β-cyclodextrin and cationic surfactant on the reaction were studied.

2. Experimental

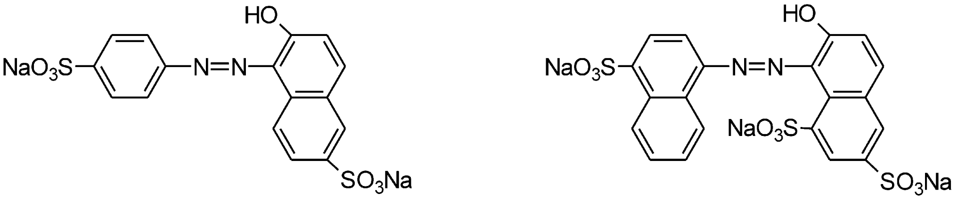
2.1. Materials

SY (E-110, C.I. 15985), 1-*p*-sulfophenylazo-2-naphthol-6-sulfonic acid disodium salt, PR (E-124, C.I. 16255), 4- sulpho-1-naphthyalazo-1-hydroxy-2-naphthalene-6,8-disulfonic acid trisodium salt, Scheme 1, Cetyltrimethylammonium bromide (CTAB), and β-cyclodextrine (β-CD) were supplied from Aldrich. Water used was doubly distilled over alkaline $KMnO_4$ in an all-glass apparatus. For the daily kinetic runs a stock solution of each dye (10^{-3} M) was prepared and the desired concentration was obtained by dilution. Sodium dithionite and sodium bisulfite were obtained from Merck. Its stock solutions were always freshly prepared to ensure constant concentration for each kinetic run and were determined as described in [23,24].

2.2. Kinetic measurements

The kinetic measurements using dithionite were conducted with Hi-Tech stopped-flow spectrophotometer (Model SF-3L, Salisbury, UK). The spectrophotometer was interfaced with an Apple IIe computer to collect data as changes in signal volt/or absorbance vs. time. The dye solution was transferred into one syringe and the other syringe was filled with dithionite solution. The delivery tubes are constructed of Teflon with an internal diameter of 1.6 mm. Each tube is approximately 40 cm long. This length of delivery tube ensures that about 0.8 cm^3 of each reagent is thermostatted prior to the stopped flow run. *Pseudo*-first order conditions of excess dithionite concentration (0.05–0.3 M) over dyes concentrations (0.5–10×10^{-4} M) was employed. The reaction was followed up in terms of changes the signal volt/or absorbance with time at $\lambda_{max} = 483$ nm and 507 nm for SY and PR dyes, respectively. The appropriate volume of others additive reagents such as: buffer, surfactant (CTAB), and β-CD were added to dye solution before getting mixed with dithionite.

With respect to the bisulfite reductant the kinetic studies were carried under *pseudo*-first order conditions in solution containing excess bisulfite concentration (0.1–0.3 M) over dye concentration (10^{-4} M). The reaction was followed up in terms of changes of absorbance with time using



Sunset Yellow (E-110, C.I. 15985)   Ponceau-4R (E-124, C.I. 16255)

Scheme 1. The structural formula of dyes investigated.

the conventional UV/Vis. spectrophotometer. The measurements were performed in 1 cm cell on a Shimadzu UV/vis. -2100S spectrophotometer. The cell holder temperature of the instrument was held constant electronically by the aid of an attached Shimadzu temperature controller (TCC-260). pH measurements were carried out with a Crison digital pH-meter (Model –501) equipped with a Crison glass electrode.

2.3. Stoichiometry

The stoichiometry of the reaction was determined spectrophotometrically by measuring the absorbance of SY and PR at $\lambda_{max} = 483$ and 507 nm, $\varepsilon = 17{,}970$ and 14,018 l mol^{-1} cm^{-1}, respectively, for a series of solutions containing constant concentration of dye while the concentration of reductant was varied. The mixtures were kept for 3 h before measurements. The [dye]:[reductant] ratio was 1:1 with each dye as shown in Eqs. (1) and (2).

$$\text{Dye} + S_2O_4^{2-} + 2H_2O \rightarrow \text{product} + 2HSO_3^- \quad (1)$$

$$\text{Dye} + S_2O_5^{2-} + H_2O \rightarrow \text{product} + 2HSO_3^- \quad (2)$$

3. Results and discussion

3.1. Reactions order and rate constant

The reduction kinetics of the present dyes using sodium dithionite were investigated by the stopped-flow spectrophotometer. On mixing dithionite and dye solutions the latter becomes colorless. The disappearance of the color as signal volt (S) vs. time is presented in Fig. 1(a). The plot of ln S vs. time is linear with negative slope, Fig. 1(b), and obeys the equation

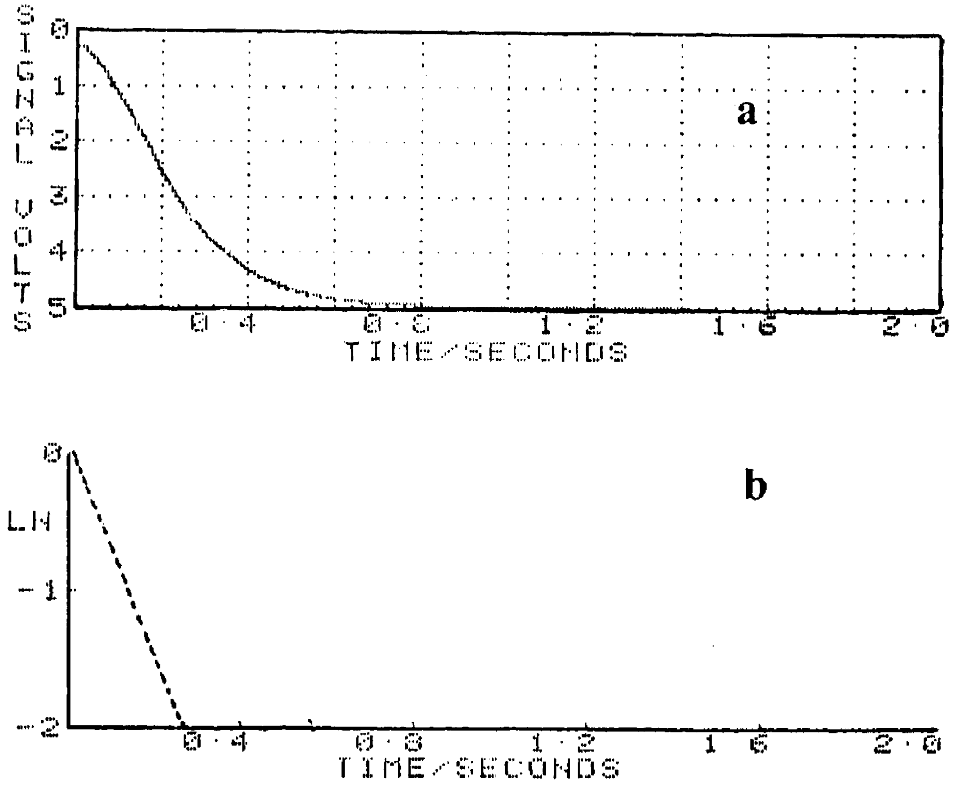


Fig. 1. (a). Typical reaction curve measured by stopped-flow spectrophotometer, [PR dye] = 10^{-3} M, [dithionite] = 0.2 M, and $t = 30$ °C. (b) First-order plot for the data given in (a).

Table 1
The rate constants and the activation parameters for the reduction of SY and PR dyes using dithionite and bisulfite in absence and presence of β-CD at different temperatures: [dithionite] = 0.2 M, [bisulfite] = 0.1 M, [SY] = 10^{-4} M, [PR] = 3×10^{-4} M, and [β-CD] = 10^{-3} M

Dye	t (°C)	k_{obs} (s^{-1})	E (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta G^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (JK/mol)
PR	22	5.11	39.42	36.90	69.13	−110.0
	26	6.20				
	30	7.86				
	34	9.28				
	38	11.72				
	42	15.87				
SY/β-CD	30	0.94	53.66	51.08	74.88	−80.0
	33	1.23				
	36	1.48				
	40	1.94				
	45	2.60				
SY	30	0.56	56.09	53.52	75.90	−80.0
	33	0.85				
	36	1.10				
	40	1.35				
	45	1.67				
PR[a]	30	0.00040	91.72	89.14	94.09	−20.0
	35	0.00076				
	40	0.00125				
	45	0.00228				
SY[a]	30	0.00085	60.83	58.25	92.99	−120.0
	35	0.00123				
	40	0.00171				
	45	0.00270				

[a] Reaction with sodium bisulfite.

$$\ln(S_\infty - S_t) = \ln S_\infty - k_{\text{obs}} t \tag{3}$$

where S_t and S_∞ refer to the signal intensity at t = t and $t = \infty$, respectively, k_{obs} is the pseudo-first order rate constant. The values of k_{obs} were reproducible and the average value is of triplicate runs. As seen in Table 1, it is clear that PR has a higher rate constant (≈10 fold) compared with SY. This can be attributed to the bonding of the azo group of SY with sulfophenyl and naphtholsulfonate moieties of the electron affinity (E_A) −1.15 and 0.15 eV, respectively [25]. While in the case of PR, the azo group is bonding with two naphthylsulfonate moieties. However, the electron density at the azo group of SY is higher than that of PR. This decreases the capability of the azo group of SY to accept electron from the reducing agent.

The reduction reaction of the dye by bisulfite was studied using conventional UV/vis spectrophotometer. The decrease in the absorption at 483 nm is consistent with the formation of a Lemon yellow color compound with an absorbance at $\lambda_{\text{max}} = 418$ nm and the appearance of two isosbestic points at 445 and 335 nm (Fig. 2). In the case of PR, two isosbestic points at 469 and 360 nm have also been viewed. The reaction obeyed first order kinetics with respect to [dye]. The plot of ln A_t vs. time (Fig. 3), gives a straight line whose slope equal to the pesudo-first order rate constant, k_{obs}, according to Eq. (4).

$$\ln A_t = \ln A_o - k_{\text{obs}} t \tag{4}$$

where A_o is the absorbance at time $t = 0$ and A_t is the absorbance at time $t = t$. The values of rate

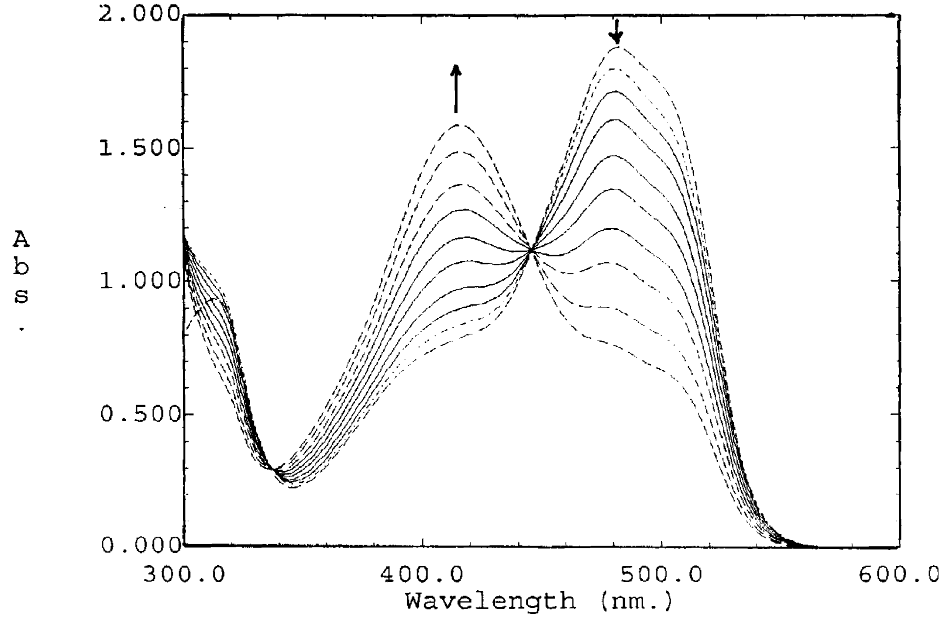


Fig. 2. Absorption spectra for the reduction of SY of 10^{-4} M with 0.1 M of bisulfite at 30 °C.

constant were determined and listed in Table 1. As can be shown, the reduction of the dye using dithionite exhibited higher rate constant (≈10,000 times) compared with bisulfite. Moreover, SY exhibited higher rate constant compared with PR. This is in contrast with that found for the reduction process using dithionite. These results prove good evidence that the reduction of both dyes using bisulfite followed a mechanism, which is different from that followed in the case of dithionite.

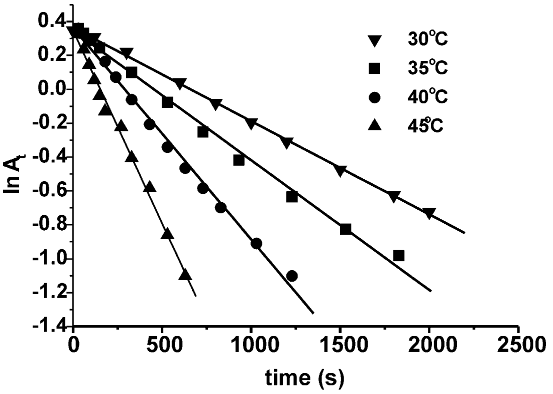


Fig. 3. First-order plot for the reaction of PR (3×10^{-4} M) with bisulfite (0.1 M) at different temperatures.

3.2. Activation parameters

The activation parameters are determined from the temperature dependence (298–318 K) of the rate constant. A plot of ln (k_{obs}/T) vs. $1/T$ [Eq. (5)] is shown in Fig. 4, where k_{obs} is the observed rate constant, K is Boltzmann constant, h is Plank constant. The enthalpy, $\Delta H^{\#}$, and entropy, $\Delta S^{\#}$,

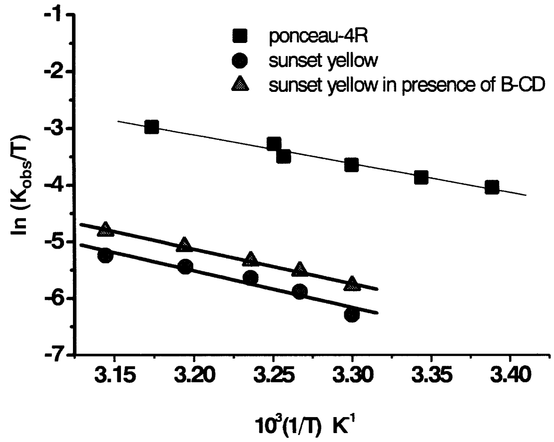


Fig. 4. Eyring's plots showing the temperature dependence for the reduction of the dyes. [SY] = 10^{-4} M, [PR] = 3×10^{-4} M, [dithionite] = 0.2 M and [β-CD] = 10^{-3} M, sweep time = 5 s.

of activation was determined from the slope and intercept, respectively, and listed in Table 1. The free energy of activation, ($\Delta G^{\#}$), was determined from Eq. (6). The average experimental temperature T was equal 305 K

$$\ln\left(\frac{k_{\mathrm{obs}}}{T}\right) = \ln\left(\frac{K}{h}\right) - \frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R} \tag{5}$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{6}$$

As shown in Table 1, the higher values of k_{obs} are associated with lower activation energy, i.e., the enthalpy is greater for the slower reaction. This suggests that the reaction is controlled by the enthalpy of activation [26,27].

3.3. Effect of [bisulfite]

The effect of bisulfite concentration on the reaction rate was investigated by maintaining the concentration of dye and temperature (30 °C) constants. The plots of k_{obs} vs. [bisulfite] were found to be linear for both dyes (corr. coeff. 0.99) with an abscissa intercepts equals 0.04 and 0.07 mol/l for PR and SY, respectively Fig. (5).

This proves that at [bisulfite]$\leqslant$0.04 and 0.07 mol/l, the reduction of the dyes does not occur. This may be attributed to the weak reducing properties of bisulfite at low concentrations. Moreover, the presence of isosbestic points indicates clearly the reversibility of this reaction and should be occurred in the presence of excess bisulfite. The linear plot of Fig. 5 indicates the first order dependence of rate constant on the bisulfite concentration. This means that the reaction obeys an overall second-order kinetics. This is in agreement with that reported elsewhere [28]. The slope is equal to 0.0158 and 0.0163 s^{-1} mol^{-1} l for PR and SY, respectively, and represent the true rates constants.

The nucleophilic attack of SY by bisulfite has been reported to be on the more accessible carbon-4 position because of its lower steric hindrance with respect to the carbon-2 (C-4) position [29–31]. This argument could also be applied in the present study. Therefore, the dyes under consideration are reduced by bisulfite via formation of the C-4 sulfonate adducts. This reaction is clearly reversible in the usual conditions (when the medium does not contain excess bisulfite as in the case of food industries). The good evidence for the existence of equilibrium between the dye and the sulfonate adducts may be obtained from the appearance of isosbestic points.

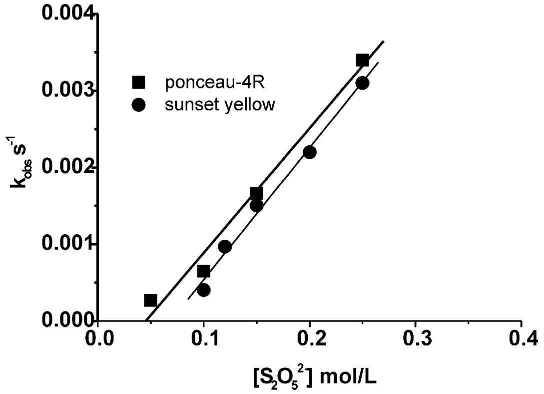


Fig. 5. Relationship between rate constant (k_{obs}) and [bisulfite] at 30 °C.

3.4. Effect of [dithionite]

The plot of k_{obs} vs. [dithionite] showed the increasing of reaction rate with increasing [$S_2O_4^{-2}$] with non-linear relation for both dyes. The order of reaction with respect to [dithionite] was determined from the logarithmic plot of ln k_{obs} vs. ln [$S_2O_4^{-2}$] (Fig. 6). The order is 0.6 and 0.58 for SY and PR dye, respectively, as was determined from

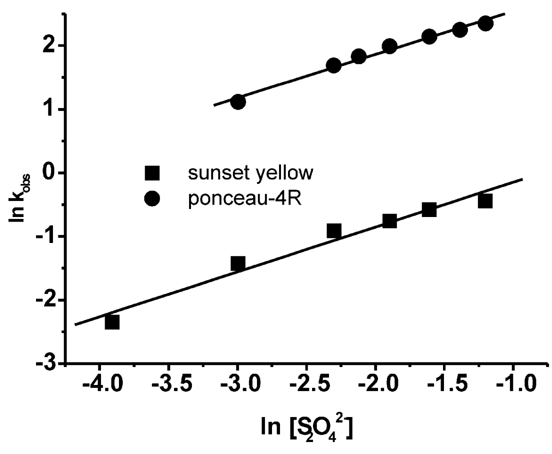


Fig. 6. Logarithmic plots of ln k_{obs} with ln [[$S_2O_4^{2-}$].

the slope. These values are closed to 0.5, half-order with respect to $[S_2O_4^{-2}]$, which is in good agreement with the rate law reported elsewhere [32]. This means that the overall order for the reduction of dyes using dithionite is 1.5. Lambeth and Palmer [20] pointed out that the kinetic reduction of different substrates using dithionite have different orders and are depended on $[S_2O_4^{-2}]$.

It is well known that dithionite could be exists in equilibrium with its dimer form and both the monomers and the dimers may act as the reducing species [13,14]. At higher $[S_2O_4^{2-}]$ the dimers is more predominant. In the present study, the concentration range of dithionite is low, hence, it could be expected that the reductant species would be the monomer. In order to verify which species, $S_2O_4^{2-}$ or $SO_2^{-\cdot}$ is more predominant, the plot of k_{obs} vs. $[S_2O_4^{2-}]^1$ was carried out as shown in Fig. 7. The linear relations shown in this figure ensure the involvement of $SO_2^{-\cdot}$ as a reducing species in the reduction mechanism. This indicates that the dithionite molecule could be dissociated to give two radical anions and the latter act as strong reducing agent. Moreover, the plots of $k_{obs}/[S_2O_4^{2-}]^{1/2}$ vs. $[S_2O_4^{2-}]^{1/2}$ showed an initial increase at low $[S_2O_4^{2-}]$ up to a maximum at ≈0.2 M of dithionite. Thus, it was followed by downward variation. These results are in contrast with the observations of Srividya et al. [10] and Lambeth and Palmer [20]. They pointed out the involvments of dithionite as reducing species. Furthermore, the involvement of $S_2O_4^{2-}$ as reductant in this study was ruled out as can be shown from the plot of $k_{obs}/[S_2O_4^{2-}]$ vs. $[S_2O_4^{2-}]^{1/2}$ which gives inverse linear relation (negative slope) Fig. (8). This reveals that the reducing species is the $SO_2^{-\cdot}$ and therefore, the reduction of dyes by radical anion is confirmed.

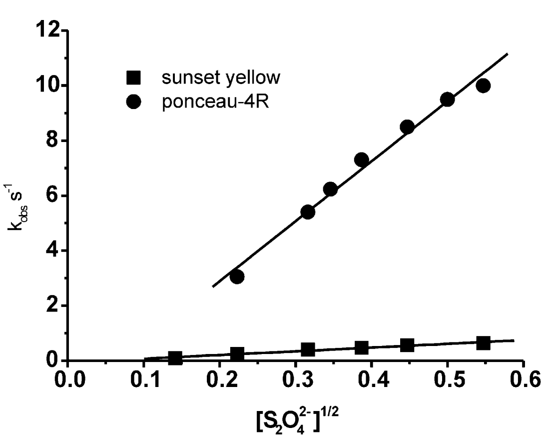


Fig. 7. Variation of k_{obs} with $[S_2O_4^{2-}]^{1/2}$ at 30 °C.

3.5. *Effect of [surfactant]*

The effect of cationic surfactant, CTAB, on the reaction rate was investigated. As shown in Fig. 9, further increases in the surfactant concentration led to decrease of the reduction rate. This retardation in the rate constant (with both dyes) could be attributed to the formation of micellar aggregates, which squeezed the dye molecules and protected

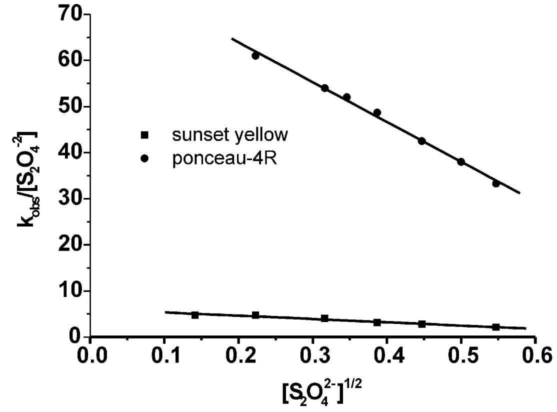


Fig. 8. Variation of k_{obs} /$[S_2O_4^{2-}]$ with $[S_2O_4^{2-}]^{1/2}$ at 30 °C.

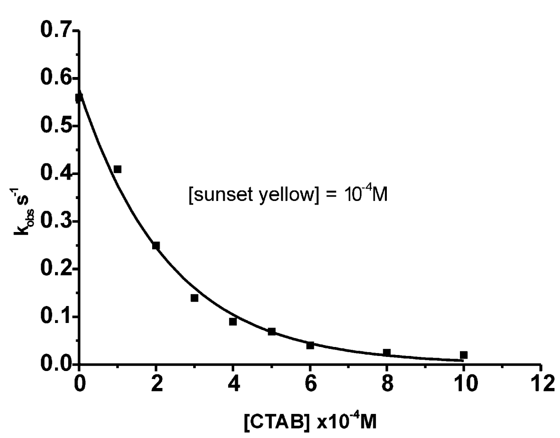


Fig. 9. Changes of the rate constant with the concentration of cationic surfactant, CTAB, [SY] = 10^{-4} M, [dithionite] = 0.2 M, t = 30 °C.

them from the nucleophilic attack, by the reducing species [33]. The CTAB concentration employed to show such effect should be around or exceeds its cmc (9×10^{-4} M) and this in fact is our finding. Another reason for decreasing the reduction rate could be due to the electrostatic interaction and the formation of ion pair between dye and the positively charged head group of CTAB monomers, Eq. (7) [34,35];

$$D^- - Na^+ + S^+ - Br^- \rightleftharpoons \underset{\text{ion pair}}{D^- - S^+} + Na^+ - Br^- \qquad (7)$$

Additional reason for the inhibiting effect of CTAB may be provided with the increase in the medium viscosity coming along with formation of micelle [36]. Consequently, the diffusion rate and the efficiency of reducing species would be decreased.

3.6. Effect of pH

Phosphate buffer was utilized to study the effect of pH variation on the reduction rate. The dependence of pseudo-first order rate constant on pH is shown in Table 2. The rate constant increases as the pH changes from 4 up to 12. These results can be attributed to that dithionite ion is unstable in dithionite in solution of pH <10. Also, it is known that at pH<7 bisulfite ions rapidly decompose and immediately forming hydrogen sulfite ion [28]. This means that the stability of both reductants is increased with raising pH. Moreover, the protonation of azo group of both dyes is more favored at lower pH, which then becomes less vulnerable to react with the reductant. The pK of both dyes have been determined and equal to 6.0 and 6.8 for SY and PR, respectively. The oxidation potential of dithionite was measured by polarography at different pHs and did not changed with varying pH and equal to + 0.355 V [10].

Table 2
Changes of the rate constant with pH for the reduction of SY and PR dyes using dithionite and bisulfite at 30 °C; $[S_2O_4^{2-}]=0.2$ M, $[S_2O_5{}^{2-}]=0.1$ M, SY $=10^{-4}$ M, and PR $=3\times10^{-4}$ M

pH	Dithionite		Bisulfite	
	SY (k_{obs} s^{-1})	PR (k_{obs} s^{-1})	SY ($k_{obs}\times10^4 s^{-1}$)	PR ($k_{obs}\times10^4 s^{-1}$)
4.5	0.51	6.50	7.12	3.12
6.0	0.53	7.00	7.85	3.30
7.5	0.58	7.40	8.30	3.80
8.5	0.65	8.50	8.90	4.50
9.5	0.70	8.70	9.20	4.90
10.5	0.73	8.90	9.60	5.10
11.0	0.75	9.00	9.90	5.30
12.0	0.76	9.05	10.20	5.50

3.7. Effect of β-CD

The effect of β-CD on the reduction rate was studied. Different concentrations of β-CD were added to the reaction medium. When SY/β-CD solution was mixed with dithionite the former became colorless immediately. As shown in Fig. 10, the value of k_{obs} increases as the concentration of β-CD increased. On the other hand, when PR/β-CD mixture was mixed with dithionite, no detectable changes of the k_{obs} were observed. The same trend was observed in the case of bisulfite. These results could be attributed to the fact that the hydrophobic cavity of β-CD is amenable to form inclusion complex with low-polarity molecules of suitable geometry. This complex involves relatively week nonspecific interactions, for example; van der Waal‘s, hydrogen bond, and hydrophobic forces. Evidence for the formation of such inclusion complex was obtained from the bathochromic shift of SY/β-CD solution i.e. λ_{max} shifted to 490

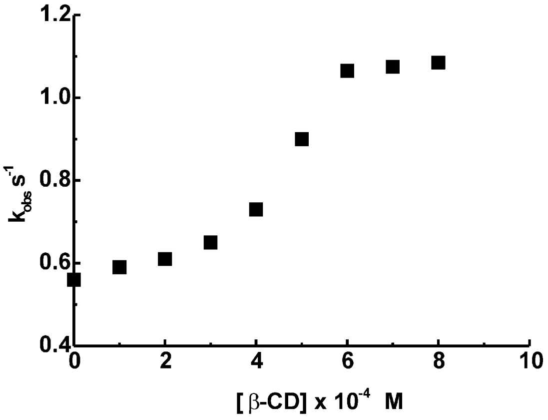


Fig. 10. Illustration of the effect of concentration of β-CD on the observed rate constant (k_{obs}) at 30 °C. [SY] $=10^{-4}$ M and [dithionite] $=0.2$ M.

nm. Whereas, with PR/β-CD solution no changes in absorption spectra was observed. As shown in Scheme 2, SY could be included inside the β-CD cavity through the *p*-sulfophenylazo side with an orientation perpendicular to the β-CD axis. In the case of PR the inclusion of naphthylsulphonate moiety is sterically impossible. Numerous data have been previously accumulated for the formation of dye/β-CD inclusion complex [37–40]. In general, CDs are known to modify the reactivity of the included molecule [38].

3.8. Reaction mechanism

3.8.1. Reduction by dithionite

Based on the above experimental observations, the reaction mechanism was proposed utilizing the reducing properties of ditionite. The initial step may involve the dissociation of dithionite into radical anions, $SO_2^{-\cdot}$. The following is a possible mechanistic scheme describing the reduction process.

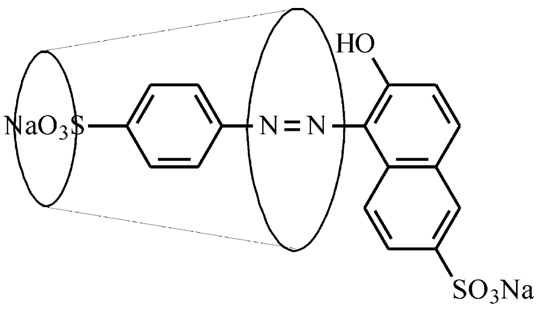
$$S_2O_4^{2-} \overset{K}{\rightleftharpoons} 2SO_2^{-\cdot} \qquad (8)$$

$$-N == N- \ +SO_2^{\cdot-} \underset{\text{slow}}{\overset{k_1}{\rightarrow}} \ -N^{\cdot}-N^{-}- +SO_2 \qquad (9)$$

$$-N^{\cdot}-N^{-}- +SO_2^{\cdot-} \underset{\text{fast}}{\overset{k_2}{\rightarrow}} \ -N^{\cdot}-N^{\cdot}+SO_2 \qquad (10)$$

$$-N^{\cdot}-N^{\cdot}- +2H_2O+2SO_2 \overset{\text{fast}}{\rightarrow} \ -NH-NH- +2HSO_3^{-} \qquad (11)$$

Thus, the rate equation can be written as following;



Scheme 2. Inclusion of SY into β-CD cavity.

$$\text{Rate} = -\frac{d[\text{dye}]}{dt} = k_1[\text{dye}][SO_2^{\cdot-}] \qquad (12)$$

From Eq. (8), the concentration of radical anion can be calculated as;

$$[SO_2^{\cdot-}]^2 = K[S_2O_4^{-}] \qquad (13)$$

or

$$[SO_2^{\cdot-}] = \sqrt{K}\ [S_2O_4^{-}]^{0.5} \qquad (14)$$

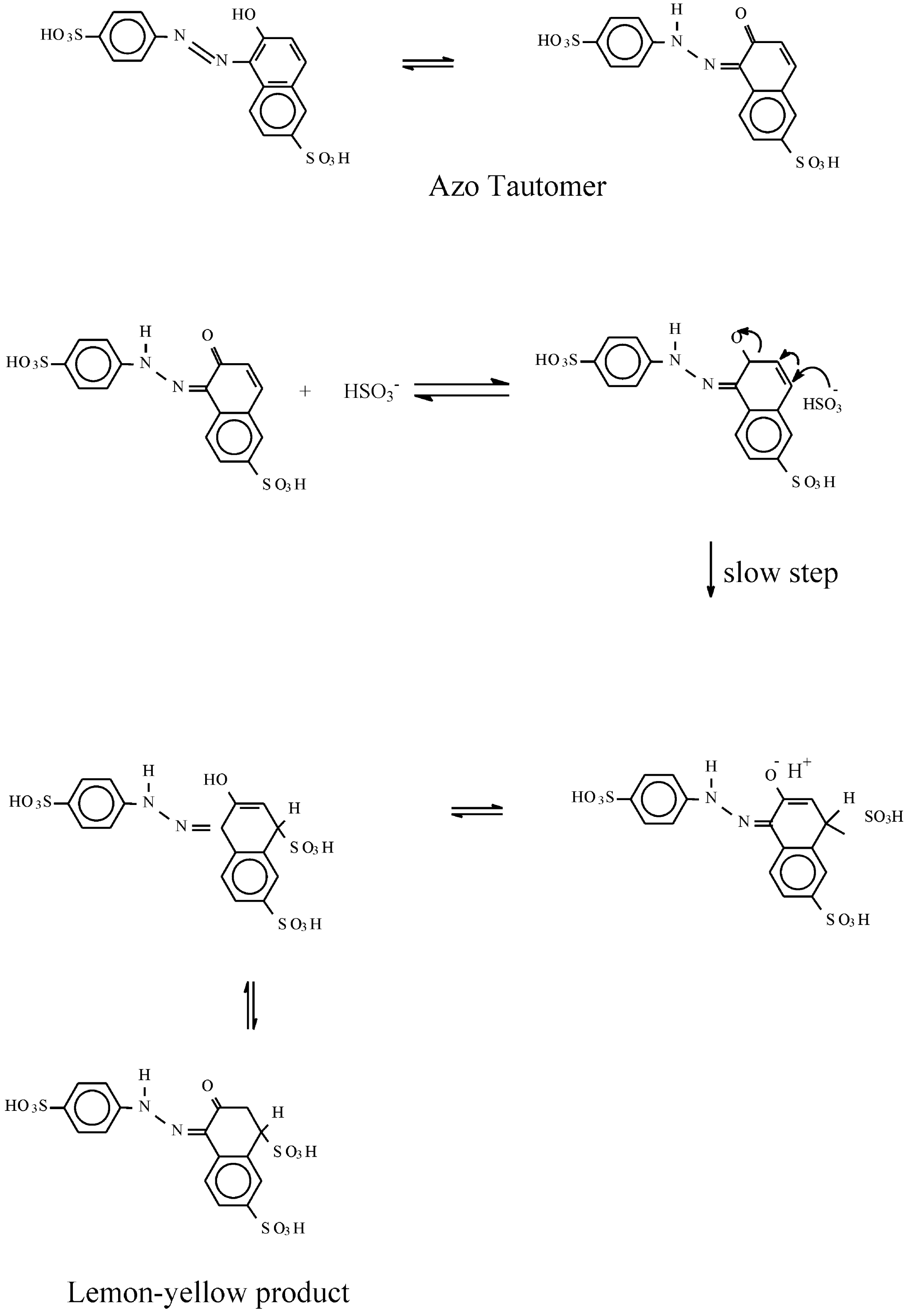
Thus, by substitution from Eq. (14) in Eq. (12) we get

$$\text{Rate} = k_1\sqrt{K}\ [\text{dye}]\ [S_2O_4^{-}]^{0.5} \qquad (15)$$

As can be seen in Eq. (15) the reaction is first order with respect to dye concentration and half-order with respect to dithionite concentration. This is in agreement with the kinetic results. Moreover, the mechanistic shown above can thus be envisaged to be in line with that reported for the electrochemical reduction of the azo dyes mentioned in [41]. The reduction products are isolated and identified by IR spectroscopy. The spectra of product showed the disappearance of the band at 1610 cm^{-1} corresponding to (–N = N–) and the appearance of broad band at 3382 cm^{-1} corresponding to –NH– group overlapped with hydroxyl group.

3.8.2. Reduction by bisulfite

In view of the experimental findings, it would seem appropriate to discuss the mechanism of the reduction by bisulfite. The formation of the product, lemon-yellow compound, and the presence of isosbestic points confirmed the sulfonation of dye at C-4, which have been characterized using HPLC, NMR, and FAB–MS spectroscopy by Damant et al. [31]. The mechanistic scheme for the reduction of SY can be proposed as shown in Scheme 3. It involves an initial equilibrium between bisulfite and hydrogen sulfite ions (Eq. 16), followed by equilibrium between hydrogen


HO3S
HO
N
N
SO3H
H
O
Azo Tautomer
HSO3-
slow step
O- H+
SO3H
Lemon-yellow product

Scheme 3.

sulfite and dye, which was confirmed by the appearance of isosbestic points. Thus, the formation of lemon yellow product is the rate- determining step (slow step).

$$S_2O_5^{2-} + H_2O \longleftrightarrow 2HSO_3^- \qquad (16)$$

4. Conclusions

In summary, SY and PR dyes were found to be very sensitive to the reduction by dithionite and bisulfite. During the reduction there was a loss in the color. Reduction using dithionite has high rate compared with bisulfite. The direct involvement of the radical anion $SO_2^{\cdot-}$ as a reducing agent was confirmed from the kinetics studies. The formation of C-4 sulfonate-adducts in the case of bisulfite reduction was suggested. Reduction rate was affected by more than one effect, the conversion was higher in alkaline medium, in the presence of β-CD, and at raising the temperature. The results revealed that there is a difference between the complete inclusion of dye as in case of surfactant and the inclusion of a part of dye, β-CD effect. Therefore, it can be concluded that the SY and PR contained in food, drugs, and cosmetics, they can subject to conditions resemble to those discussed above. During storage their prone to the bleaching should be diminished by avoiding the presence of reducing agents.

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