

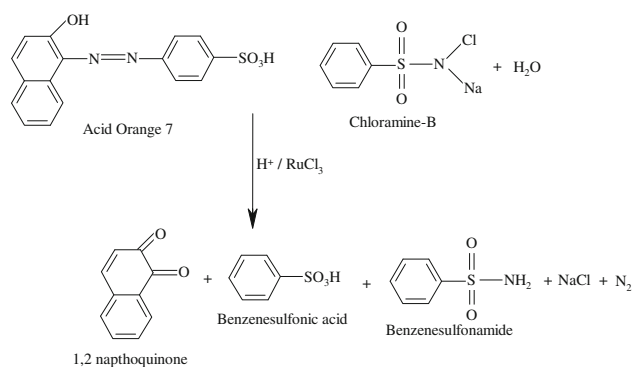
RuCl₃ Catalyzed and Uncatalyzed Oxidative Decolorization of Acid Orange 7 Dye with Chloramine-B in Acid Medium: Spectrophotometric, Kinetic and Mechanistic Study

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Abstract Acid orange 7, chemically known as sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene)hydrazinyl]benzenesulfonate, is extensively used for dyeing textiles, paper and leather. The discharge of wastewater containing this dye, causes environmental and health related problems. Therefore, in the present research, we have developed optimum conditions for the facile oxidative decolorization of this dye with sodium N-chlorobenzenesulfonamide or chloramine-B (CAB). The kinetics and mechanism of oxidative decolorization of acid orange 7 dye with CAB in acidic medium have also been studied spectrophotometrically at 303 K in the presence and absence of RuCl₃ catalyst. Under similar experimental conditions, the reaction exhibits a first-order dependence of rate each on [CAB]₀ and [dye]₀, and an inverse-fractional-order dependence on [H⁺] for both the RuCl₃ catalyzed and uncatalyzed reactions. The order with respect to RuCl₃ is fractional. Activation parameters have been computed. Dielectric effect is negative in both the cases. Oxidation products of the acid orange 7 dye are identified as 1,2-naphthoquinone and benzenesulfonic acid by GC–MS data. The RuCl₃ catalyzed reaction is about four fold faster than the uncatalyzed reaction. The chemical oxygen demand value of the dye was determined. The mechanistic pathways and kinetic modelings have been computed based on experimental results. The developed oxidative decolorization method is expected to be helpful to treat acid orange 7 dye present in wastewater after suitable modifications.

Graphical Abstract The stoichiometry of the reaction is in the mole ratio of 1:1(AO7:CAB) in both the cases as shown given below



Keywords Chloramine-B · Acid orange 7 · RuCl₃-catalysis · Oxidative-decolorization · Kinetics-mechanism

1 Introduction

Acid orange 7 is chemically known as sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene)hydrazinyl]benzenesulfonate and it is widely used for dyeing textiles, paper and leather [1, 2]. The industrial wastewater bearing this dye causes environment and health problems. Oxidation decolorization is considered a simple and economic technology for the removal of dyestuffs from wastewater. Though there are many reports in literature on the oxidative decolorization of this dye [3–5], similar studies have not yet been carried out by keeping its kinetic and mechanistic aspects. The chemistry of organic N-haloamines is of great interest due to their diverse behavior [6]. The important chloramine compounds of this class are sodium N-chloro-p-toluenesulfonamide or

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chloramine-T (CAT) and sodium N-chlorobenzenesulfonamide or chloramine-B (CAB). The mechanistic aspects of many of these reactions have been documented [7–16]. The decolorization of acid orange 7 dye was tested with both CAT and CAB in acid medium. It was observed that the decolorization of this dye is most effective with CAB.

To the best of our knowledge, the impact of platinum group metal ions on the oxidation of acid orange 7 dye has not yet been investigated. Among platinum group metal ions, ruthenium (III) chloride (RuCl_3) has been extensively employed as a homogeneous catalyst in redox reactions [17–19] and some of these systems have proved suitable for kinetic analysis [20–23]. Our preliminary experimental results indicated that a micro-quantity of RuCl_3 effectively catalyzes the oxidation of acid orange 7 dye with CAB in acid medium. Therefore, in the present work, we have explored the kinetics and mechanism of the acid orange 7—CAB redox system in acid medium in the absence and presence of RuCl_3 catalyst. The other objective of the present study is to optimize the reaction conditions for the efficient decolorization of acid orange 7 dye with CAB in acid medium.

2 Experimental and Methods

2.1 Materials and Reagents

Chloramine-B was obtained from Sigma and purified by the method of Morris et al. [24]. An aqueous solution of CAB was prepared afresh whenever required, standardized by iodometric method and stored in brown bottles until further use to prevent its any photochemical deterioration. Acid Orange 7 (SD Fine Chem. Ltd., India) was used as received and an aqueous solution of the desired strength of the dye was prepared afresh each time. A solution of RuCl_3 (Merck) was prepared in 20 mM HCl and employed as a catalyst. Allowance was made for the

amount of acid present in the catalyst solutions while preparing reaction mixtures for kinetic runs. All the chemicals used were of analytical grade and used as such. All the solutions were prepared using double distilled water.

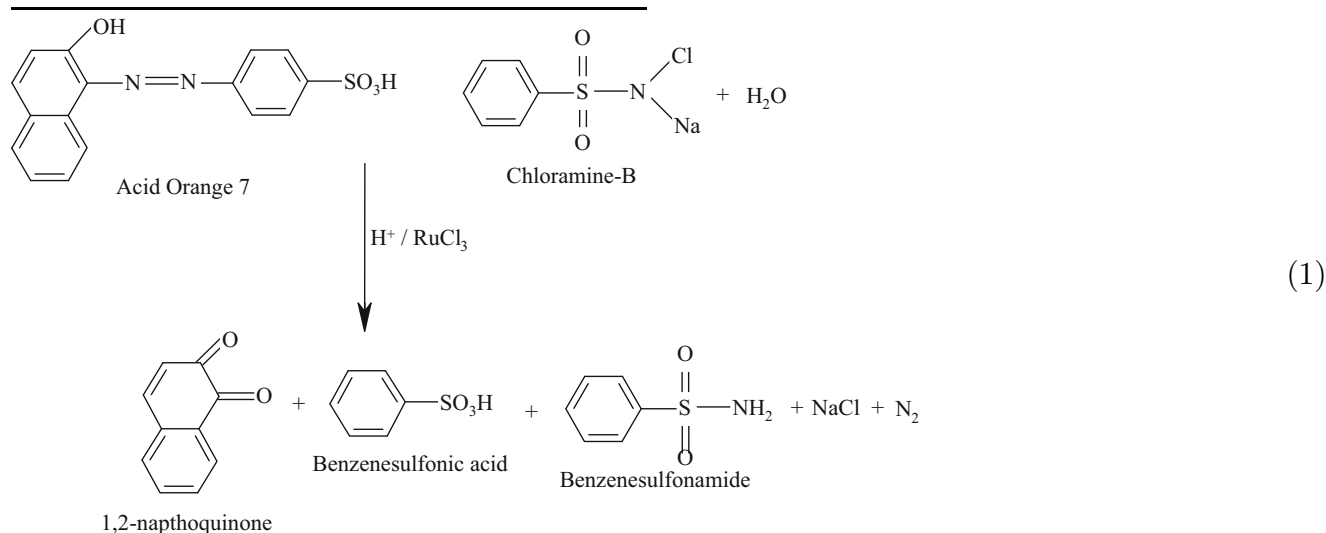
2.2 Kinetic Measurements

Kinetic measurements were carried out using a UV–Vis spectrophotometer. (SL 159. Elico Ltd). Kinetic runs were performed under pseudo-first-order conditions by keeping an excess of CAB over dye in HClO_4 medium with and without RuCl_3 at 303 K and the detailed procedure which was followed is similar to that reported earlier [25]. Absorbance measurements were made at 484 nm (λ_{max} for the dye) for more than two half-lives. The absorbance readings at $t = 0$ and $t = t$ are D_0 and D_t and plots of $\log D_0/D_t$ versus time were made to evaluate the pseudo-first-order rate constants (k' s^{-1}). All the kinetic runs were carried out twice to check the reproducibility, and was found to be reproducible within $\pm 5\%$ error. Calculations of the regression coefficients (R^2) were carried out using fx—100 W scientific calculator.

3 Results

3.1 Reaction Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined by equilibrating varying ratios of $[\text{CAB}]_0$ and $[\text{dye}]_0$ in presence of $3.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ HClO}_4$ ($2.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ RuCl}_3$ for the catalyzed reaction) at 303 K for 24 h. Determination of the residual oxidant showed that the stoichiometry of the reaction is in the mole ratio of 1:1 in both the cases as shown in Eq. 1.



The reaction mixture in the stoichiometric ratio was allowed to progress for 24 h in the presence of HClO₄ (RuCl₃ for the catalyzed reaction) at 303 K under stirred conditions. After completion of the reaction (monitored by TLC), the reaction products were neutralized with dilute NaOH and extracted with ethyl acetate. Separation of these products was achieved using silica gel (60–100 mesh) column chromatography with hexane/ethyl acetate (8:6, v/v) as mobile phase. The oxidation products were identified as 1,2-naphthoquinone and benzenesulfonic acid for the RuCl₃ catalyzed and uncatalyzed reactions. These are confirmed by GC–MS analysis. GC–MS data were obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectra showed a molecular ion peak at 158 and 158 amu, clearly conforming 1,2-naphthoquinone and benzenesulfonic acid, respectively. It was also noticed that there was no further reaction of these oxidation products under the present set of experimental conditions. Benzenesulfonamide (BSA or PhSO₂NH₂), the reduction product of CAB, was detected [26] by TLC using light petroleum-chloroform-butan-1-ol (2:2:1 v/v/v) as the solvent and iodine for detection. The R_f value was found to be 0.88, which is in good agreement with the literature value [26]. Nitrogen was detected by the conventional test.

3.2 Kinetic Orders

The kinetics of oxidative decolorization of acid orange-7 (hereafter abbreviated as dye) with CAB has been

investigated spectrophotometrically at several initial concentrations of the reactants in HClO₄ medium with and without RuCl₃ catalyst. The standard experimental conditions established for the facile oxidative decolorization of the dye are: [CAB]₀ = 3.0 × 10^{−3} mol dm^{−3}, [dye]₀ = 2.0 × 10^{−4} mol dm^{−3}, [HClO₄] = 3.0 × 10^{−3} mol dm^{−3}, and [RuCl₃] = 2.0 × 10^{−5} mol dm^{−3} (in case of catalyzed reaction) at T = 303 K. Under these conditions, CAB decolorizes the dye completely within 25 and 90 min in the presence and absence of RuCl₃ catalyst. The pseudo-first order rate constants obtained for standard run in the presence and absence of RuCl₃ catalyst are 16.2 × 10^{−4} and 3.80 × 10^{−4} s^{−1}, respectively. Hence, it can be said that RuCl₃ acts as an effective catalyst for the facile oxidative decolorization of acid orange-7 by CAB in acid medium. Unless otherwise noted, the other attributes of the reactions were unchanged by the presence of RuCl₃.

The kinetic runs were performed under pseudo-first-order conditions of [CAB]₀ ≫ [dye]₀ in both the cases. At constant [CAB]₀, [HClO₄], RuCl₃ (in case of catalyzed reaction) and temperature, plots of log(absorbance) versus time were linear (R² > 0.9884), indicating a first-order dependence of rate on [dye]₀ for both RuCl₃ catalyzed and uncatalyzed reactions. The values of pseudo-first order rate constants (k' s^{−1}) were found to be independent of [dye]₀, confirming the first-order dependence of rate on [dye]₀. The values are given in Table 1. The rate increased with the increase in [CAB]₀ (Table 1) in both the cases and log–log plots of rate

Table 1 Effect of varying [CAB]₀, [Dye]₀, [HClO₄] and [RuCl₃] on the rate of reaction at 303 K

[CAB] ₀ × 10 ³ (mol dm ^{−3})	[AO7] ₀ × 10 ⁴ (mol dm ^{−3})	[HClO ₄] × 10 ³ (mol dm ^{−3})	[RuCl ₃] × 10 ⁵ (mol dm ^{−3})	k' × 10 ⁴ (s ^{−1})	
				Uncatalyzed	RuCl ₃ catalyzed
0.5	2.0	3.0	2.0	0.52	2.52
1.0	2.0	3.0	2.0	1.64	5.75
3.0	2.0	3.0	2.0	3.80	16.2
6.0	2.0	3.0	2.0	11.2	32.0
10.0	2.0	3.0	2.0	16.5	53.3
3.0	0.5	3.0	2.0	3.79	16.2
3.0	1.0	3.0	2.0	3.81	16.1
3.0	2.0	3.0	2.0	3.80	16.2
3.0	4.0	3.0	2.0	3.82	16.3
3.0	8.0	3.0	2.0	3.81	16.1
3.0	2.0	0.5	2.0	18.6	31.4
3.0	2.0	1.0	2.0	14.8	25.2
3.0	2.0	3.0	2.0	3.80	16.2
3.0	2.0	6.0	2.0	2.43	10.2
3.0	2.0	12.0	2.0	1.32	7.81
3.0	2.0	3.0	0.5	–	8.06
3.0	2.0	3.0	1.0	–	11.3
3.0	2.0	3.0	2.0	–	16.2
3.0	2.0	3.0	4.0	–	23.2
3.0	2.0	3.0	8.0	–	30.7

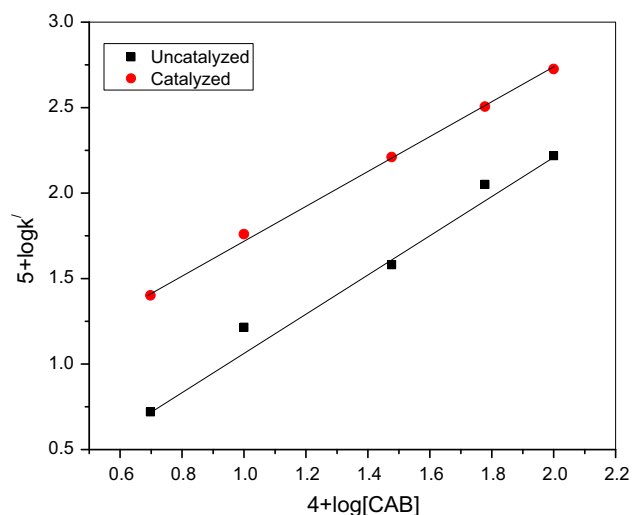


Fig. 1 Plots of $\log k'$ versus $\log [CAB]_0$

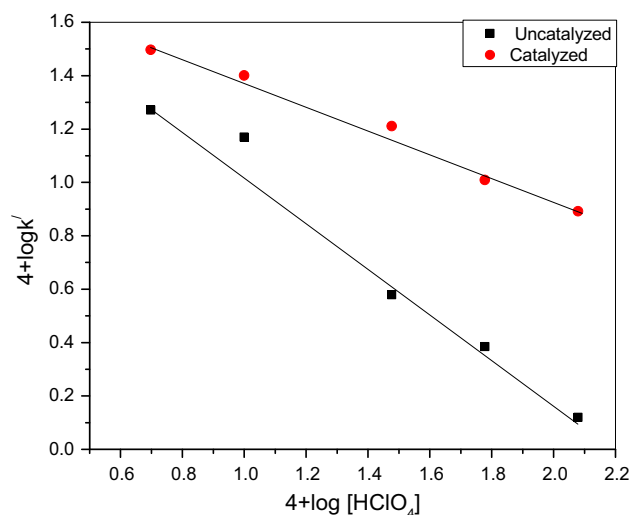


Fig. 2 Plots of $\log k'$ versus $\log [HClO_4]$

versus $[CAB]$ were linear (Fig. 1; $R^2 > 0.9926$) with a slope of unity. This ensures that the kinetics exhibits a first-order dependence on $[CAB]_0$. Further, plots of k' versus $[CAB]$ were linear ($R^2 > 0.9939$) passed through the origin, confirming the first-order dependence of rate on $[CAB]_0$ and also showing the transient nature of the intermediate formed with the dye.

The reaction rate decreased with increase in $[HClO_4]$ (Table 1) and plots of $\log k'$ versus $\log [HClO_4]$ were linear (Fig. 2; $R^2 > 0.9904$) with fractional slopes of -0.50 and -0.86 for $RuCl_3$ catalyzed and uncatalyzed reactions, respectively. This clearly indicates a negative fractional-order dependence of rate on $[HClO_4]$ in both the cases. The rate increased with an increase in $[RuCl_3]$ (Table 1) and the

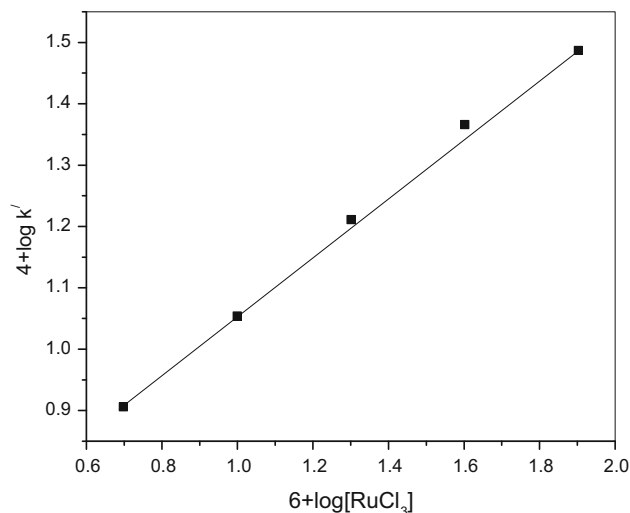


Fig. 3 Plots of $\log k'$ versus $\log [RuCl_3]$

Table 2 Effect of varying dielectric constant of the medium on the rate of reaction at 303 K

% MeOH (v/v)	D	$k' \times 10^4 \text{ (s}^{-1}\text{)}$	
		Uncatalyzed	$RuCl_3$ catalyzed
0	76.73	3.80	16.2
10	72.37	2.69	14.8
20	67.48	1.65	12.3
30	62.71	0.93	10.1

Experimental conditions: $[CAB]_0 = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[dye]_0 = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[HClO_4] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$; and in catalyzed reaction $[RuCl_3] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$

slope of $\log k'$ versus $\log [RuCl_3]$ plot (Fig. 3; $R^2 = 0.9990$) was found to be 0.48, indicating a fractional-order dependence of rate on $[RuCl_3]$. The dielectric constant of the medium was varied using different amounts of methanol and H_2O (0–30 % v/v). The reaction rate decreases with an increase in methanol content in both the cases (Table 2). Plots of $\log k'$ versus $1/D$ were found to be linear (Fig. 4; $R^2 > 0.9960$) with negative slopes. Values of dielectric constant of methanol–water mixture reported in literature were employed [27]. Blank experiments performed showed that MeOH was not oxidized significantly by CAB under the prevailing experimental conditions (without substrate). No attempt was made to keep the ionic strength of the system fixed for both the reactions, since the pseudo-first-order rate constants remains unaltered in presence of 0.2 mol dm^{-3} $NaClO_4$ solution.

Addition of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ benzenesulfonamide (BSA or $PhSO_2NH_2$), the reduction product of CAB, to the reaction mixture showed negligible influence on the rate of the reaction in both the cases. It signifies that the BSA is not

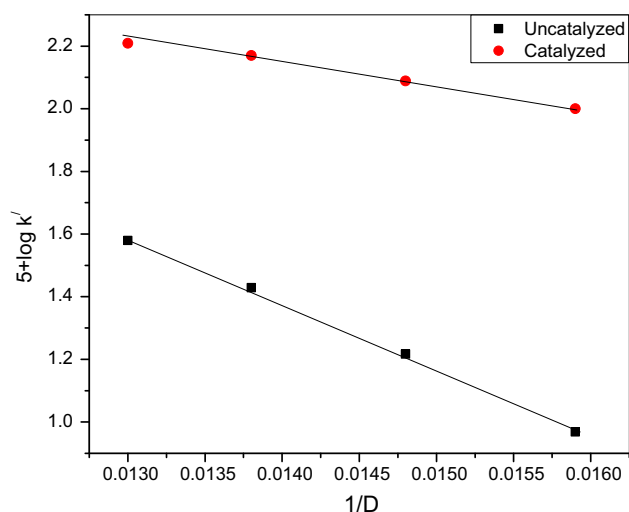


Fig. 4 Plots of $\log k'$ versus $1/D$

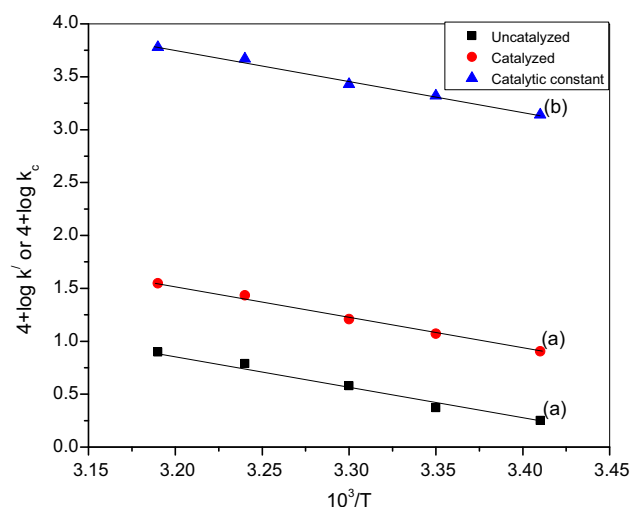


Fig. 5 Plots of (a) $\log k'$ versus $1/T$ and (b) $\log K_C$ versus $1/T$

involved in any step prior to the rate determining steps (rds) in the reaction schemes. Similarly, addition of Cl^- ion in the form of NaCl ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) does not have any

pronounced effect on the rate of the reaction, indicating that the Cl^- ion plays no role in the reaction sequence. Activation parameters (E_a , $\Delta H^\ddagger$, $\Delta G^\ddagger$, $\Delta S^\ddagger$ and $\log A$) for the reaction have been evaluated from Arrhenius plots of $\log k'$ versus $1/T$ (Fig. 5; $R^2 > 0.9939$) by studying the reactions at different temperatures (293–313 K). These results are summarized in Table 3. On adding a small amount of the reaction mixture to acrylonitrile, there was no polymerization indicating the absence of free radical species in the reaction sequence.

4 Discussion

As CAT and CAB exhibit similar chemical properties, it is expected that identical equilibria exist in aqueous solutions of these compounds [28, 29]. In general, CAB undergoes a two electron change in its reactions [30]. The redox potential of CAB/BSA couple is pH dependent and decreases with increase in pH of the medium [30].

4.1 Reactive Species of CAB

Chloramine-B ($\text{PhSO}_2\text{NClNa}$) behaves as a strong electrolyte [28] and depending on the pH of the medium, it furnishes different equilibria in aqueous solutions [24, 28, 29]. The possible oxidizing species in acidified CAB solutions are PhSO_2NHCl , $\text{PhSO}_2\text{NCl}_2$, HOCl and possibly $\text{H}_2\text{O}^+\text{Cl}$, and in alkaline solutions they are PhSO_2NHCl , $\text{PhSO}_2\text{NCl}^-$, HOCl and OCl^- . The present redox system was carried out in acid medium and hence from the four possibilities, the reactive species of CAB can be decided based on the observed kinetic data.

4.2 Tautomerism of Acid Orange 7 Dye

Azo dyes, such as Acid Orange 7, containing hydroxyl groups conjugated to azo group [31] exhibit azo-hydrazone tautomerism as shown below:

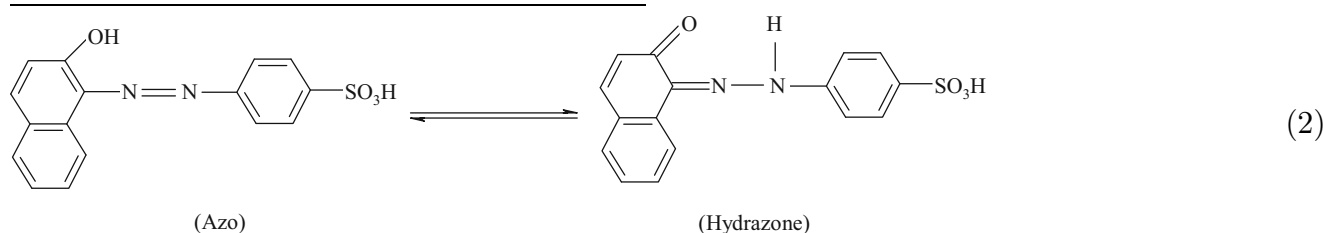


Table 3 Temperature dependence and activation parameters for the oxidative decolorization of AO 7 by CAB in acid medium in the presence and absence of RuCl₃ catalyst

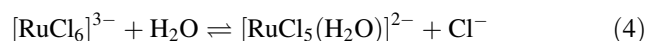
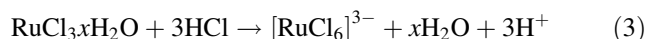
Temperature (K)	$k' \times 10^4$ (s ⁻¹)		Kc
	Uncatalyzed	RuCl ₃ -catalyzed	
293	1.79	8.02	0.14
298	2.35	11.8	0.21
303	3.80	16.1	0.27
308	6.14	27.1	0.47
313	7.92	35.2	0.61
E_a (kJ mol ⁻¹)	70.1	55.3	55.0
$\Delta H^\ddagger$ (kJ mol ⁻¹)	67.8 (±0.06)	52.8 (±0.01)	52.4 (±0.01)
$\Delta G^\ddagger$ (kJ mol ⁻¹)	94.1 (±0.20)	90.4 (±0.15)	52.5 (±0.01)
$\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	-87.6 (±0.04)	-124 (±0.09)	-82.6 (±0.01)
Log A	12.0 (±0.27)	11.5 (±0.01)	13.7 (±0.02)

Experimental conditions: [CAB]₀ = 3.0×10^{-3} mol dm⁻³; [dye]₀ = 2.0×10^{-4} mol dm⁻³; [HClO₄] = 3.0×10^{-3} mol dm⁻³; and in catalyzed reaction [RuCl₃] = 2.0×10^{-5} mol dm⁻³

In the present studies, the azo form of acid orange 7 is involved in the reaction.

4.3 Reactive Species of RuCl₃

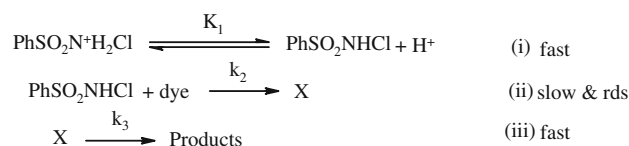
RuCl₃ catalysis in redox reactions involves different degrees of complexity, due to formation of different intermediate complexes, free radicals and its variable oxidation states. Cady and Connick [32], and Connick and Fine [33] have investigated aqueous RuCl₃ complex species using the ion exchange resins and UV-spectral studies. They found that the octahedral complex species [RuCl₅(H₂O)]²⁻, [RuCl₃(H₂O)₃], [RuCl₂(H₂O)₄]⁺ and [RuCl(H₂O)₅]²⁺ may not exist in aqueous solution of RuCl₃. Other studies [17, 34, 35] have shown the existence of following equations for RuCl₃ in acidic solutions:



In the present study, the absence of chloride ion on the rate indicates that the equilibrium (4) does not play any role in the reaction. Hence, the complex ion, [RuCl₅(H₂O)]²⁻, is assumed to be the reactive catalyst species.

4.4 Reaction Scheme and Rate Law for Uncatalyzed Reaction

The probable reactive species in acidic solutions of CAB are PhSO₂NHCl, PhSO₂NCl₂, HOCl and possibly H₂O⁺Cl. The first-order dependence of rate on [CAB]₀ and the addition of PhSO₂NH₂ (benzenesulfonamide) having no effect on the reaction rate both indicate that PhSO₂NCl₂ and HOCl may not be the reactive species. Hardy and Johnston [29], who have studied the pH-dependent relative concentrations of the species present in acidified CAB

**Scheme 1** A general reaction Scheme for the oxidative decolorization of acid orange 7 with CAB in acid medium

solutions of comparable molarities and have shown that PhSO₂NHCl is the likely oxidizing species in acid medium. Narayanan and Rao [36] and, Subhashini et al. [37] have reported that CAB can further be protonated at pH < 2 to give PhSO₂N⁺H₂Cl. In the present case, protonated oxidant (PhSO₂N⁺H₂Cl) generates the free conjugate acid (PhSO₂NHCl) in the acid retarding step and hence PhSO₂NHCl is the active oxidizing species. In view of these points, Scheme 1 can be formulated for the oxidation of acid orange 7 dye with CAB in acidic medium.

Here X is the complex intermediate species whose structure is shown in Scheme 2. In Scheme 2, in an initial equilibrium [step(i)], deprotonation of PhSO₂N⁺H₂Cl generates the conjugate free acid PhSO₂NHCl. In the next slow and rds [step(ii)], the azo form of the dye reacts with the conjugate acid of the oxidant to form the dye-CAB complex (X) with the elimination of PhSO₂NH₂. The complex X in the presence of a molecule of water through the several fast steps [step(iii)] yields the ultimate products viz., 1,2-naphthoquinone and benzenesulfonic acid with the elimination of a molecule each of HCl and N₂.

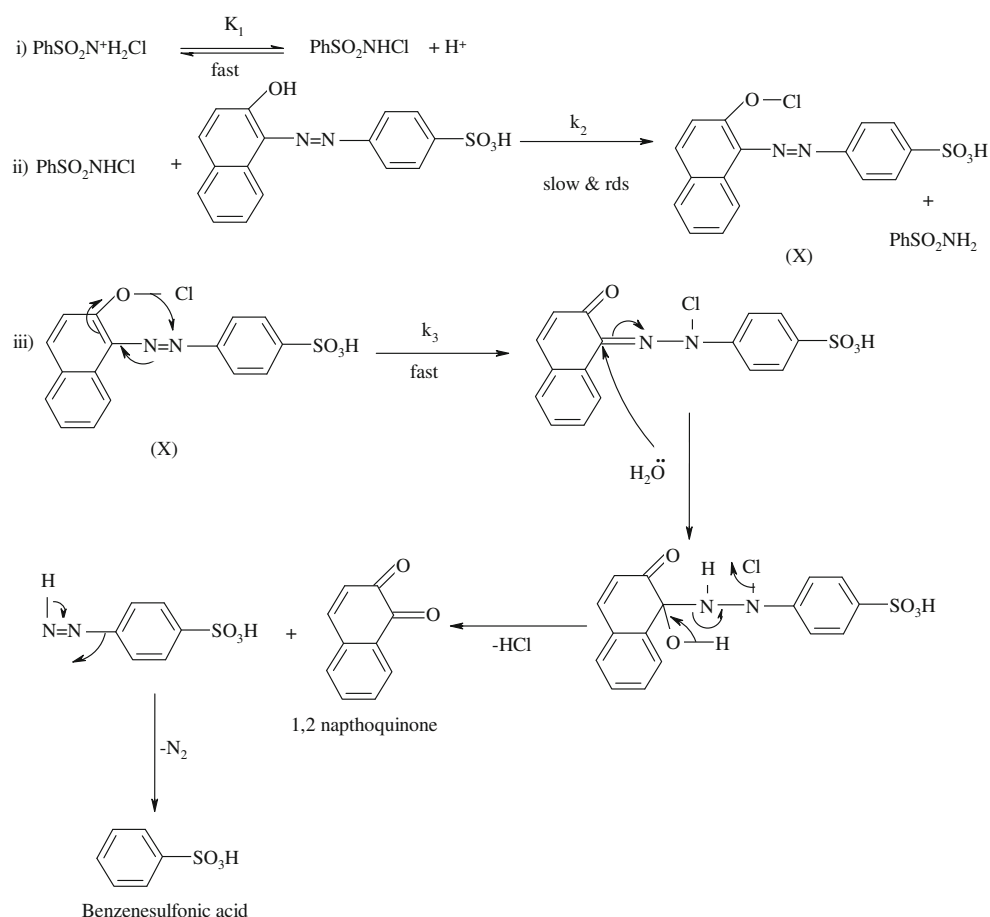
If [CAB]_t is the total effective concentration of CAB, then based on Scheme 1, we can write

$$[\text{CAB}]_t = [\text{PhSO}_2\text{N}^+\text{H}_2\text{Cl}] + [\text{PhSO}_2\text{NHCl}] \quad (5)$$

From step (i) of Scheme 1,

$$[\text{PhSO}_2\text{N}^+\text{H}_2\text{Cl}] = \frac{[\text{PhSO}_2\text{NHCl}][\text{H}^+]}{K_1} \quad (6)$$

Scheme 2 A detailed mechanistic interpretation for the oxidative decolorization of acid orange 7 with CAB in acid medium



On substituting the value of $\text{PhSO}_2\text{N}^+\text{H}_2\text{Cl}$ from Eq. 6 into Eq. 5, and solving for PhSO_2NHCl , we get

$$[\text{PhSO}_2\text{NHCl}] = \frac{K_1[\text{CAB}]t}{[\text{H}^+] + K_1} \quad (7)$$

From slow/rds of Scheme 1,

$$\text{Rate} = k_2[\text{PhSO}_2\text{NHCl}][\text{dye}] \quad (8)$$

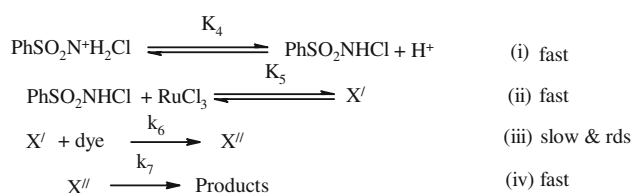
On substituting for $[\text{PhSO}_2\text{NHCl}]$ from Eq. 7 into Eq. 8, the rate of reaction is given as

$$\text{Rate} = \frac{K_1 k_2 [\text{CAB}] t [\text{dye}]}{[\text{H}^+] + K_1} \quad (9)$$

Rate law 9 holds good agreement with the experimental results, wherein a first-order dependence of rate each on $[\text{CAB}]_0$ and $[\text{dye}]_0$, and an inverse-fractional order on $[\text{H}^+]$ was noted.

4.5 Reaction Scheme and Rate Law for RuCl₃ Catalyzed Reaction

The reactive oxidizing species in this case also PhSO_2NHCl , which accounts for the observed inverse-fractional-



Scheme 3 A general reaction Scheme for the RuCl₃ catalyzed oxidative decolorization of acid orange 7 dye with CAB in acid medium

order dependence of rate on $[\text{H}^+]$. The proposed mechanism for RuCl₃ catalyzed oxidation of acid orange 7 by CAB in acidic medium is presented in Scheme 3.

Here X' and X'' represent the complex intermediate species whose structures are shown in Scheme 4. In Scheme 4, in the initial equilibrium [step(i)] deprotonation of $\text{PhSO}_2\text{NH}_2\text{Cl}^+$ generates the conjugate free acid PhSO_2NHCl . In the next fast pre-equilibrium step [step(ii)], the donor nitrogen atom of the oxidizing species coordinates to the metal centre of the active catalyst species and gives an intermediate complex X' . In the next slow and rds step [step (iii)], another intermediate complex X'' is formed from the reaction between X' and dye.

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described by Bronsted and Bjerrum theory [42]. In the present investigations, in both the cases, neutral molecules are involved in the rate determining steps of Schemes 2 and 4. Hence, variation of the ionic strength of the medium does not alter the rate in both the cases clearly conform to the above theory [42].

4.8 Catalytic Activity of RuCl₃

The general equation relating for uncatalyzed and catalyzed reactions have been derived from Moelwyn – Hughes [43] and can be correlated as:

$$k_1 = k_0 + K_C[\text{catalyst}]^x \quad (14)$$

Here k_1 is the observed pseudo-first-order rate constant obtained in the presence of RuCl₃ catalyst, k_0 is that for the uncatalyzed reaction, K_C is the catalytic constant and x is the order of the reaction with respect to RuCl₃. In the present case, x value for the standard run was found to be 0.48 for RuCl₃ catalyst. Then the K_C has been evaluated using the equation:

$$K_C = (k_1 - k_0)/[\text{RuCl}_3]^{0.48} \quad (15)$$

The values of K_C have been evaluated at different temperatures (293, 298, 303, 308 and 313 K), and K_C was found to vary with temperature. Further, a plot of $\log K_C$ versus $1/T$ was linear (Fig. 5; $R^2 = 0.9972$) and values of energy of activation and other activation parameters with respect to RuCl₃ catalyst were evaluated. All these results are tabulated in Table 3.

4.9 Comparison of RuCl₃ Catalyzed and Uncatalyzed Reactions

RuCl₃ catalyzed oxidative decolorization of the dye by CAB with that of uncatalyzed reaction (without RuCl₃ catalyst) under an identical set of experimental conditions was compared. The observed rates of oxidative decolorization of the dye in the presence of RuCl₃ catalyst revealed that the reactions are about four-fold faster than the uncatalyzed reactions (Table 3). This was also confirmed by the calculated activation energies. The difference in activation energies for the catalyzed and uncatalyzed reactions explained the catalytic effect on the rate of the reaction. This may be attributed to the formation of the intermediate complex X' between RuCl₃ and the oxidant, which increases the oxidizing property of the oxidant than without RuCl₃ catalyst. Further, RuCl₃ favorably modifies the reaction path by stabilizing the transition state, which in turn provides an alternative pathway having lower activation energy for the reaction. Consequently, it can be said that RuCl₃ is an efficient catalyst for the present redox system.

4.10 Activation Parameters

The variation of rate constants with temperatures and values of activation parameters are shown in Table 3. Values of $\Delta H^\ddagger$ indicates that the reactions are enthalpy controlled. The more positive values of $\Delta G^\ddagger$ points out a highly solvated transition state. The large negative values of $\Delta S^\ddagger$ signifies that the transition state is more rigid than the initial state with less degrees of freedom. The values of frequency factor ($\log A$) specify the frequency of collisions and orientation of the reaction molecules.

4.11 Determination of Chemical Oxygen Demand Value

In the present research, an effort has been made to determine the chemical oxygen demand (COD) for acid orange 7 dye. COD is a measure of oxidizable matter in dye stuff. The COD of acid orange 7 dye was determined using the standard dichromate method. The procedure followed to determine COD value was according to a literature procedure [44]. Under the prevailing experimental conditions, COD of acid orange 7 dye sample was found to be 1168.10 mg/lit.

5 Conclusion

Different kinetic conditions were experimented and better optimum conditions were established, for the facile oxidative decolorization of acid orange 7 dye with CAB. The rate laws obtained are: $-d[\text{CAB}]/dt = k[\text{CAB}]_0 [\text{dye}]_0 [\text{H}^+]^{-0.50} [\text{RuCl}_3]^{0.48}$ for RuCl₃ catalyzed reaction and $-d[\text{CAB}]/dt = k[\text{CAB}]_0 [\text{dye}]_0 [\text{H}^+]^{-0.86}$ for uncatalyzed reaction. Activation parameters have been evaluated. 1,2-naphthoquinone and benzenesulfonic acid were identified as the oxidation products of acid orange 7 dye. RuCl₃ catalyzed reaction is about four-fold faster than the uncatalyzed reaction. Based on the kinetic results, reaction mechanisms and rate laws have been worked out. The COD value of acid orange 7 dye was also determined. The present redox-system can be adopted for treating acid orange 7 dye present in industrial wastewater with suitable modifications to minimize the toxicity caused by it.

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References

1. Zollinger H (1981) Color chemistry: synthesis, properties and applications of organic dyes and pigments. VCH, New York

2. Silva JP, Sousa S, Rodrigues J, Antunes H, Porter JJ, Goncalves I, Ferreira-Dias S (2004) *Sep Purify Technol* 40:309–315 and references therein
3. Li G, Wang N, Liu B, Zhang X (2009) *Desalination* 249:936–941
4. Yang S, Yang X, Shao X, Niu R, Wang L (2011) *J Hazard Mater* 186(1):659–666
5. Chen X, Qiao X, Wang D, Lin J, Chen J (2007) *Chemosphere* 67(4):802–808
6. Campbell MM, Johnson G (1978) *Chem Rev* 78:65–79
7. Banerji KK, Jayaram B, Mahadevappa DS (1987) *J Sci Ind Res* 46:65–76
8. Armesto XL, Canle L, Garia MV, Santaballa JA (1998) *Chem Soc Rev* 27:453–460
9. Agnihotri G (2005) *Synlett* 18:2857–2858
10. Kolaveri E, Ghorbeni-Choghamarani A, Salehi P, Shirini F, Zolfogol MA (2007) *J Iran Chem Soc* 4:126–174
11. Vinod KN, Puttaswamy, Gowda KNN (2009) *Inorg Chim Acta* 362:2044–2051
12. Puttaswamy, Sukhdev A, Shubha JP (2012) *Prog React Kinet Mech* 37:42–58
13. Puttaswamy, Jagadeesh RV (2006) *Int J Chem Kinet* 38:48–56
14. Puttaswamy, Jagadeesh RV (2005) *Eur J Chem* 3:482–501
15. Puttaswamy, Shubha JP (2008) *Prog React Kinet Mech* 33:313–330
16. Puttaswamy, Sukhdev A (2009) *Indian J Chem* 48:339–345
17. Griffith WP (1967) *The chemistry of rare platinum metals*. Interscience, New York
18. Cotton FA, Wilkinson G, Murillo CA, Bochmann M (1999) *Advanced inorganic chemistry*, 6th edn. Wiley, New York
19. Mallesh RT, Bellakki MB, Nandibewoor ST (2004) *Catal Lett* 97:91–98
20. Bhat KR, Jyothi K, Gowda BT (2002) *Oxid Commun* 25:117–141 and references therein
21. Rashmi R, Sushma G, Upadhyay SK (1990) *Indian J Chem* 29A:847–851
22. Mulla RM, Hiremath GC, Nandibewoor ST (2004) *Monatshefte fur Chemie* 135:1489–1502
23. Jagadeesh RV, Puttaswamy (2008) *J Phys Org Chem* 21:844–858
24. Morris JC, Salazar JA, Wineman MA (1948) *J Am Chem Soc* 70:2036–2041
25. Puttaswamy, Shubha JP, Jagadeesh RV (2007) *Trans Met Chem* 32:991–999
26. Venkatesha BM, Ananda S, Mahadevappa DS (1992) *J Phys Org Chem* 5:373–381
27. Akerloff G (1932) *J Chem Soc* 54:4125–4139
28. Bishop E, Jennings VJ (1958) *Talanta* 1:197–199
29. Hardy FF, Johnston JP (1973) *J Chem Soc Perkin Trans* 2:742–745
30. Murthy ARV, Rao BS (1952) *Proc Ind Acad Sci* 35:69–72
31. Oakes J, Gratton P (1998) *J Chem Soc Perkin Trans* 2:2201 and reference therein
32. Cady HH, Connick RE (1958) *J Am Chem Soc* 80:2646–2652
33. Connick RE, Fine DA (1960) *J Am Chem Soc* 82:4187–4192
34. Backhouse JR, Dwyer FD, Shales N (1950) *Proc R Soc* 83:146–155
35. Davfokratova T (1963) *Analytical chemistry of ruthenium*. Academy of Sciences, USSR
36. Narayanan SS, Rao VRS (1983) *Radiochem Acta* 32:211–212
37. Subhashini M, Subramanian M, Rao VRS (1985) *Talanta* 32:1082–1085
38. Amis ES, Jaffe G (1942) *J Chem Phys* 10:598–604
39. Laidler KJ, Landskroener PA (1956) *Trans Faraday Soc* 52:200–210
40. Tanford C, Kirkwood JG (1957) *J Am Chem Soc* 79:5333–5339
41. Reiherdt C (2003) *Solvent and solvent effects in organic chemistry*, 3rd edn. Wiley, New York
42. Laidler KJ (1995) *Chemical kinetics*, 2nd edn. Tata Mc-Graw Hill, New Delhi
43. Moelwyn-Hughes EA (1947) *Kinetics of reactions in solutions*. Oxford University Press, London
44. Gomati Devi L, Mohan Reddy K (2010) *Appl Surf Sci* 256:3116–3122