

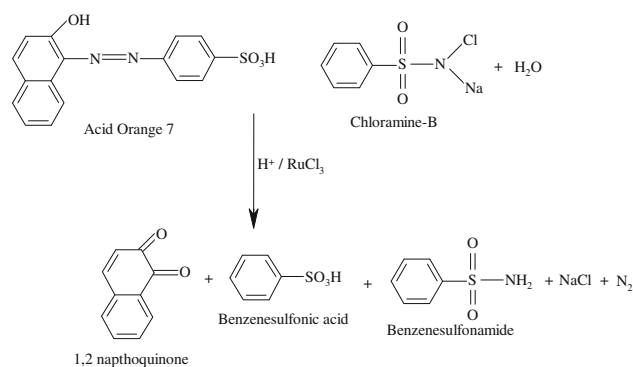
# RuCl<sub>3</sub> Catalyzed and Uncatalyzed Oxidative Decolorization of Acid Orange 7 Dye with Chloramine-B in Acid Medium: Spectrophotometric, Kinetic and Mechanistic Study

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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 RuCl<sub>3</sub> catalyst. Under similar experimental conditions, the reaction exhibits a first-order dependence of rate each on [CAB]<sub>0</sub> and [dye]<sub>0</sub>, and an inverse-fractional-order dependence on [H<sup>+</sup>] for both the RuCl<sub>3</sub> catalyzed and uncatalyzed reactions. The order with respect to RuCl<sub>3</sub> 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 RuCl<sub>3</sub> 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 · RuCl<sub>3</sub>-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. Oxidative 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<sub>3</sub>) 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> (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.

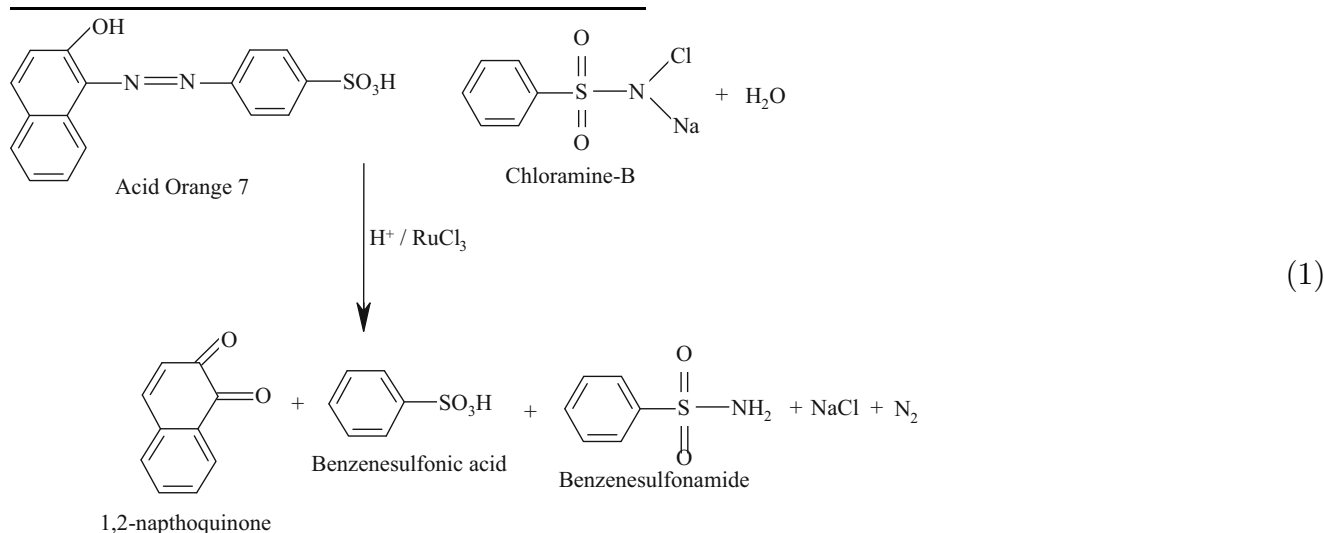
### 2.2 Kinetic Measurements

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<sub>4</sub> medium with and without RuCl<sub>3</sub> at 303 K and the detailed procedure which was followed is similar to that reported earlier [25]. Absorbance measurements were made at 484 nm ( $\lambda_{\text{max}}$  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 ( $k' \text{ s}^{-1}$ ). 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  $\text{HClO}_4$  ( $\text{RuCl}_3$  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  $\text{NaOH}$  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  $\text{RuCl}_3$  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  $\text{PhSO}_2\text{NH}_2$ ), 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

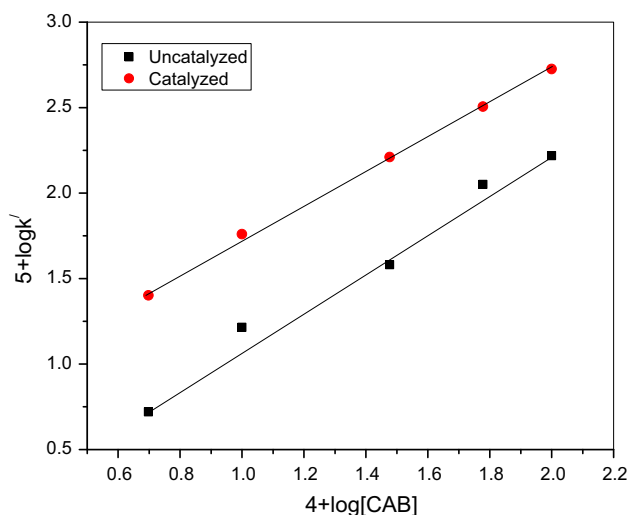
The kinetics of oxidative decolorization of acid orange-7 (hereafter abbreviated as dye) with CAB has been

investigated spectrophotometrically at several initial concentrations of the reactants in  $\text{HClO}_4$  medium with and without  $\text{RuCl}_3$  catalyst. The standard experimental conditions established for the facile oxidative decolorization of the dye are:  $[\text{CAB}]_0 = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{dye}]_0 = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and  $[\text{RuCl}_3] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$  (in case of catalyzed reaction) at  $T = 303 \text{ K}$ . Under these conditions, CAB decolorizes the dye completely within 25 and 90 min in the presence and absence of  $\text{RuCl}_3$  catalyst. The pseudo-first order rate constants obtained for standard run in the presence and absence of  $\text{RuCl}_3$  catalyst are  $16.2 \times 10^{-4}$  and  $3.80 \times 10^{-4} \text{ s}^{-1}$ , respectively. Hence, it can be said that  $\text{RuCl}_3$  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  $\text{RuCl}_3$ .

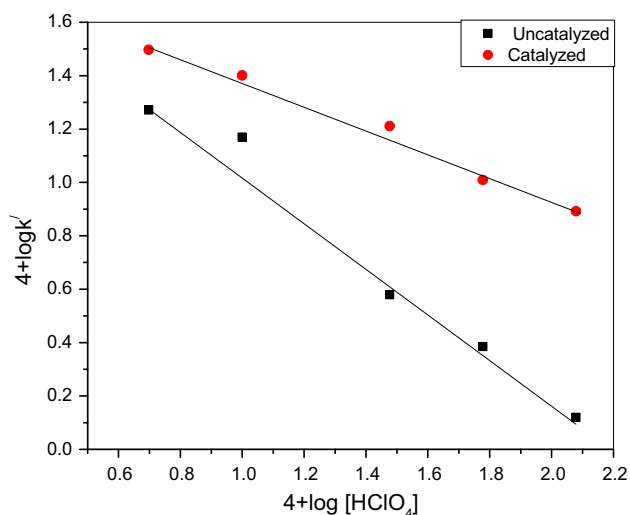
The kinetic runs were performed under pseudo-first-order conditions of  $[\text{CAB}]_0 \gg [\text{dye}]_0$  in both the cases. At constant  $[\text{CAB}]_0$ ,  $[\text{HClO}_4]$ ,  $\text{RuCl}_3$  (in case of catalyzed reaction) and temperature, plots of  $\log(\text{absorbance})$  versus time were linear ( $R^2 > 0.9884$ ), indicating a first-order dependence of rate on  $[\text{dye}]_0$  for both  $\text{RuCl}_3$  catalyzed and uncatalyzed reactions. The values of pseudo-first order rate constants ( $k' \text{ s}^{-1}$ ) were found to be independent of  $[\text{dye}]_0$ , confirming the first-order dependence of rate on  $[\text{dye}]_0$ . The values are given in Table 1. The rate increased with the increase in  $[\text{CAB}]_0$  (Table 1) in both the cases and  $\log$ – $\log$  plots of rate

**Table 1** Effect of varying  $[\text{CAB}]_0$ ,  $[\text{Dye}]_0$ ,  $[\text{HClO}_4]$  and  $[\text{RuCl}_3]$  on the rate of reaction at 303 K

	$[\text{CAB}]_0 \times 10^3$ ( $\text{mol dm}^{-3}$ )	$[\text{AO7}]_0 \times 10^4$ ( $\text{mol dm}^{-3}$ )	$[\text{HClO}_4] \times 10^3$ ( $\text{mol dm}^{-3}$ )	$[\text{RuCl}_3] \times 10^5$ ( $\text{mol dm}^{-3}$ )	$k' \times 10^4$ ( $\text{s}^{-1}$ )	
					Uncatalyzed	$\text{RuCl}_3$ 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



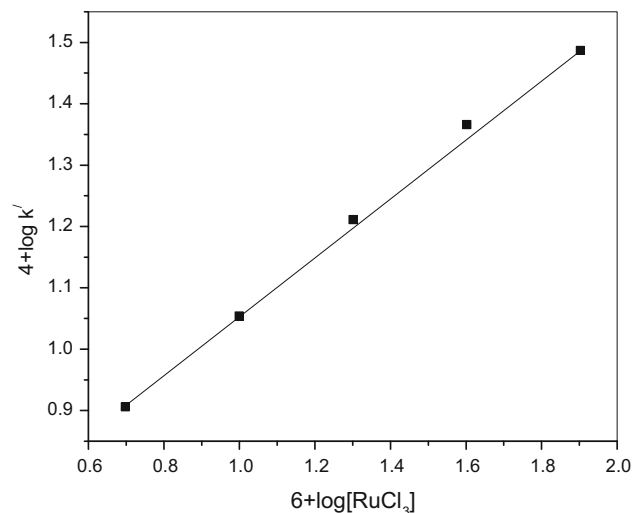
**Fig. 1** Plots of  $\log k'$  versus  $\log [CAB]_0$



**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	$k' \times 10^4$ (s <sup>-1</sup> )	
		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:  $[CAB]_0 = 3.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $[dye]_0 = 2.0 \times 10^{-4}$  mol dm<sup>-3</sup>;  $[HClO_4] = 3.0 \times 10^{-3}$  mol dm<sup>-3</sup>; and in catalyzed reaction  $[RuCl_3] = 2.0 \times 10^{-5}$  mol dm<sup>-3</sup>

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<sub>2</sub>O (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<sup>-3</sup> NaClO<sub>4</sub> solution.

Addition of  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> benzenesulfonamide (BSA or PhSO<sub>2</sub>NH<sub>2</sub>), 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

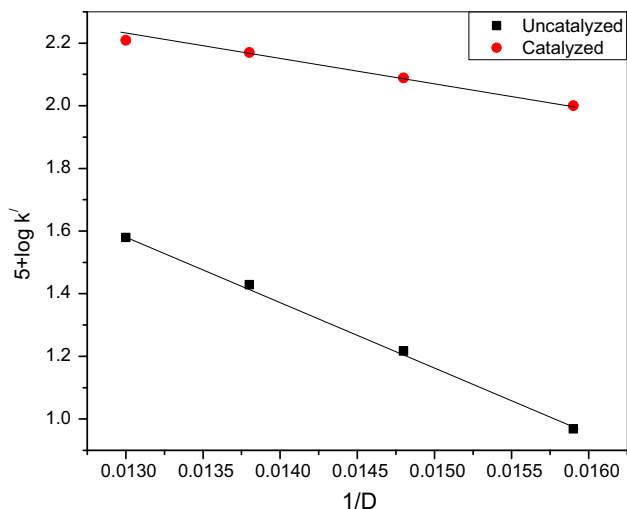


Fig. 4 Plots of  $\log k'$  versus  $1/D$

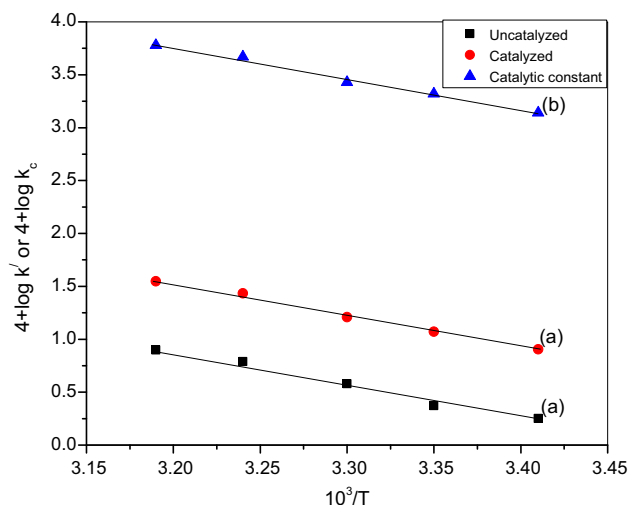
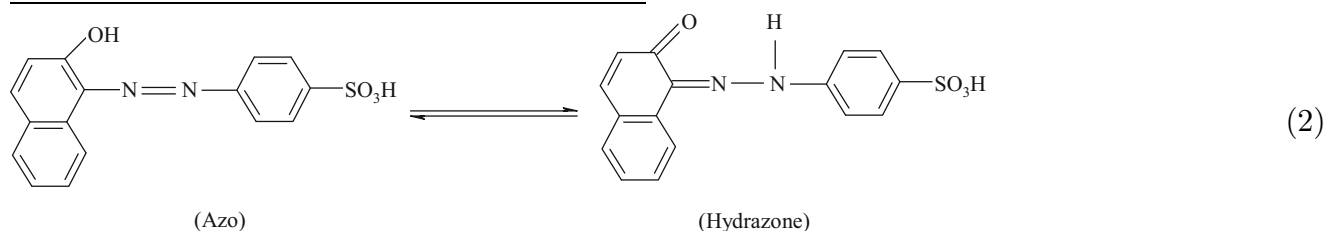


Fig. 5 Plots of (a)  $\log k'$  versus  $1/T$  and (b)  $\log K_C$  versus  $1/T$

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



pronounced effect on the rate of the reaction, indicating that the  $\text{Cl}^-$  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 ( $\text{PhSO}_2\text{NCINa}$ ) 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  $\text{PhSO}_2\text{NHCl}$ ,  $\text{PhSO}_2\text{NCl}_2$ ,  $\text{HOCl}$  and possibly  $\text{H}_2\text{O}^+\text{Cl}$ , and in alkaline solutions they are  $\text{PhSO}_2\text{NHCl}$ ,  $\text{PhSO}_2\text{NCl}^-$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ . 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 RuCl<sub>3</sub> catalyst

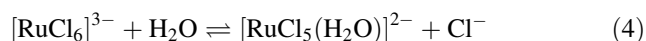
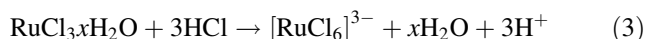
Temperature (K)	$k' \times 10^4$ (s <sup>-1</sup> )		Kc
	Uncatalyzed	RuCl <sub>3</sub> -catalyzed	
293	1.79	8.02	0.14
298	2.35	11.8	0.21
303	3.80	16.1	0.27
308	6.14	27.1	0.47
313	7.92	35.2	0.61
$E_a$ (kJ mol <sup>-1</sup> )	70.1	55.3	55.0
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	67.8 ( $\pm 0.06$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

Experimental conditions: [CAB]<sub>0</sub> =  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [dye]<sub>0</sub> =  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [HClO<sub>4</sub>] =  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>; and in catalyzed reaction [RuCl<sub>3</sub>] =  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup>

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

### 4.3 Reactive Species of RuCl<sub>3</sub>

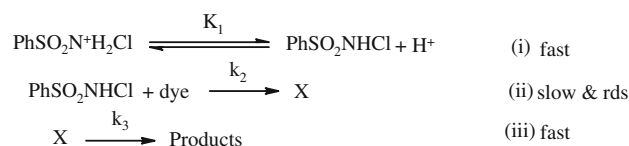
RuCl<sub>3</sub> catalysis in redox reactions involves different degrees of complexity, due to formation of different intermediate complexes, free radicals and its variable oxidation states. Cady and Connick [32], and Connick and Fine [33] have investigated aqueous RuCl<sub>3</sub> complex species using the ion exchange resins and UV-spectral studies. They found that the octahedral complex species [RuCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>, [RuCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>], [RuCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> and [RuCl(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> may not exist in aqueous solution of RuCl<sub>3</sub>. Other studies [17, 34, 35] have shown the existence of following equations for RuCl<sub>3</sub> 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, [RuCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>, 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 PhSO<sub>2</sub>NHCl, PhSO<sub>2</sub>NCl<sub>2</sub>, HOCl and possibly H<sub>2</sub>O<sup>+</sup>Cl. The first-order dependence of rate on [CAB]<sub>0</sub> and the addition of PhSO<sub>2</sub>NH<sub>2</sub> (benzenesulfonamide) having no effect on the reaction rate both indicate that PhSO<sub>2</sub>NCl<sub>2</sub> 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 PhSO<sub>2</sub>NHCl 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 PhSO<sub>2</sub>N<sup>+</sup>H<sub>2</sub>Cl. In the present case, protonated oxidant (PhSO<sub>2</sub>N<sup>+</sup>H<sub>2</sub>Cl) generates the free conjugate acid (PhSO<sub>2</sub>NHCl) in the acid retarding step and hence PhSO<sub>2</sub>NHCl 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 PhSO<sub>2</sub>N<sup>+</sup>H<sub>2</sub>Cl generates the conjugate free acid PhSO<sub>2</sub>NHCl. 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 PhSO<sub>2</sub>NH<sub>2</sub>. 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 N<sub>2</sub>.

If [CAB]<sub>t</sub> is the total effective concentration of CAB, then based on Scheme 1, we can write

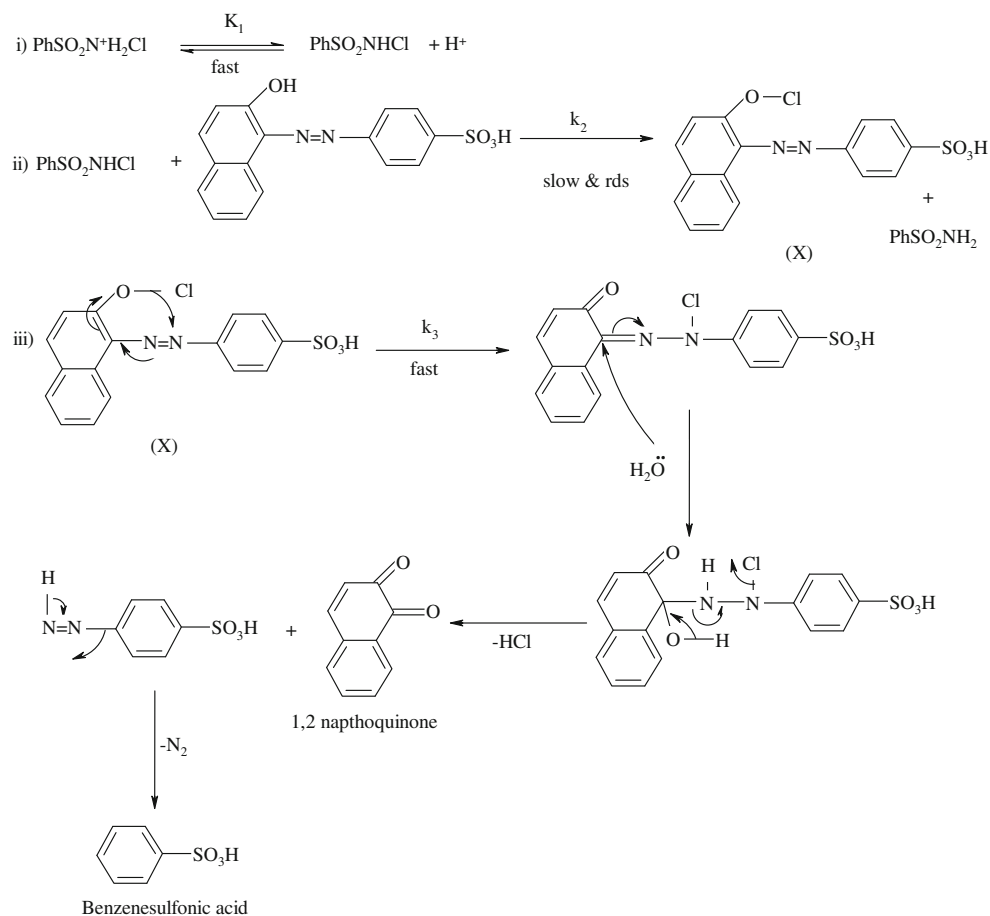
$$[\text{CAB}]_t = [\text{PhSO}_2\text{N}^+\text{H}_2\text{Cl}] + [\text{PhSO}_2\text{NHCl}] \quad (5)$$

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  $\text{PhSO}_2\text{NHCl}$ , 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,

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

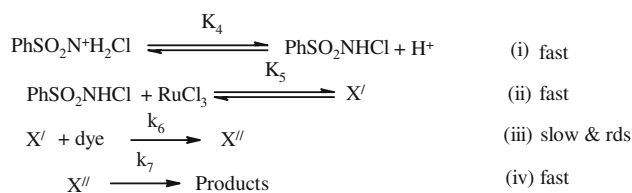
On substituting for  $[\text{PhSO}_2\text{NHCl}]$  from Eq. 7 into Eq. 8, the rate of reaction is given as

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

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 $\text{RuCl}_3$ Catalyzed Reaction

The reactive oxidizing species in this case also  $\text{PhSO}_2\text{NHCl}$ , which accounts for the observed inverse-fractional-

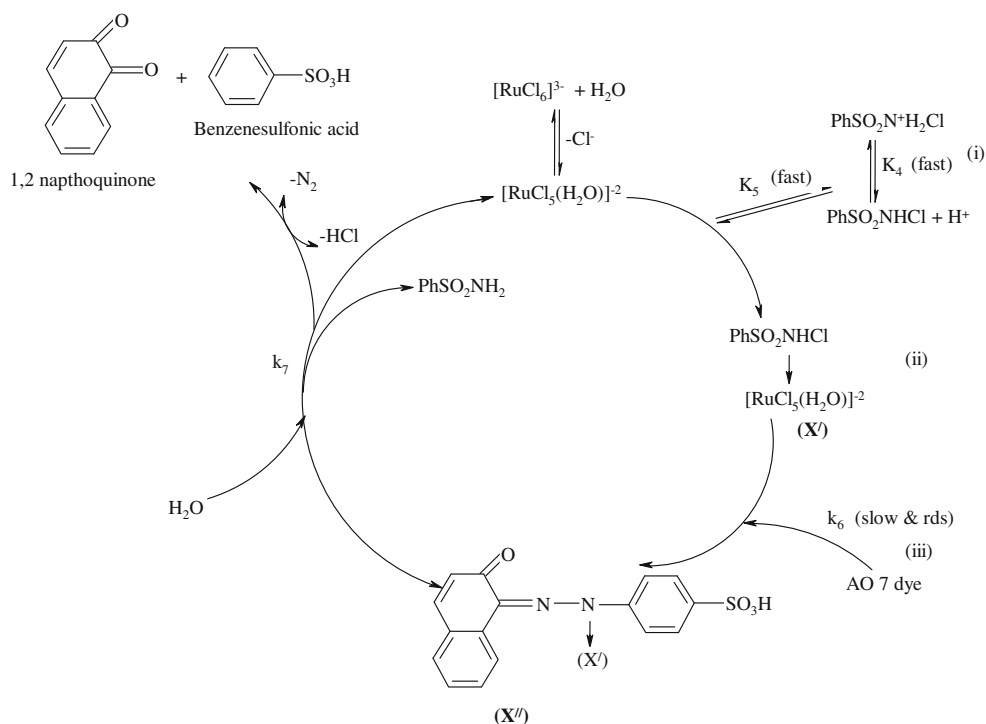


**Scheme 3** A general reaction Scheme for the  $\text{RuCl}_3$  catalyzed oxidative decolorization of acid orange 7 dye with CAB in acid medium

order dependence of rate on  $[\text{H}^+]$ . The proposed mechanism for  $\text{RuCl}_3$  catalyzed oxidation of acid orange 7 by CAB in acidic medium is presented in Scheme 3.

Here  $\text{X}'$  and  $\text{X}''$  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  $\text{PhSO}_2\text{NHCl}$ . 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  $\text{X}'$ . In the next slow and rds step [step (iii)], another intermediate complex  $\text{X}''$  is formed from the reaction between  $\text{X}'$  and dye.

**Scheme 4** A detailed mechanistic interpretation for RuCl<sub>3</sub> catalyzed oxidative decolorization of acid orange 7 dye with CAB in acid medium



Finally, the complex  $X''$  undergoes decomposition through several fast steps in the presence of  $H_2O$ , yielding the final products 1,2-naphthoquinone and benzenesulfonic acid with the elimination of  $PhSO_2NH_2$ ,  $RuCl_3$ ,  $HCl$  and  $N_2$ .

Evidence for the formation of complex between oxidant and catalyst is obtained from the UV–Visible spectra of CAB,  $RuCl_3$  and the mixture of both. Absorption maxima appear at 224 nm for CAT, 215 nm for  $RuCl_3$  in aqueous acidic medium, and 230 nm for their mixture. A bathochromic shift of 15 nm from 215 to 230 nm of  $RuCl_3$  suggests that complexation occurs between CAB and  $RuCl_3$  in the present case.

Based on the above Scheme 3, the total CAB concentration is

$$[CAB]_t = [PhSO_2N^+H_2Cl] + [PhSO_2NHCl] + [X'] \quad (10)$$

By substituting for  $[PhSO_2N^+H_2Cl]$  and  $[PhSO_2NHCl]$  from steps (i) and (ii) of Scheme 3 and solving for  $X'$ , we get

$$[X'] = \frac{K_4 K_5 [CAB]_t [RuCl_3]}{[H^+] + K_4 + K_4 K_5 [RuCl_3]} \quad (11)$$

From slow/rds of Scheme 3,

$$Rate = k_6 [dye] [X'] \quad (12)$$

By substituting for  $[X']$  from Eq. 11 into Eq. 12 we get

$$Rate = \frac{K_4 K_5 k_6 [CAB]_t [dye] [RuCl_3]}{[H^+] + K_4 + K_4 K_5 [RuCl_3]} \quad (13)$$

Rate law 13 is in accordance with the experimental findings. The proposed schemes and the derived rate laws in both the cases are also substantiated by the experimental observations discussed below:

#### 4.6 Effect of Dielectric Constant

In order to find out the nature of reactive species, the dielectric constant ( $D$ ) of the medium was varied by adding different amounts of methanol (0–30 % v/v) to the reaction mixture. The rate decreased with increasing methanol content (Table 2). Several approaches [38–41] have been made to explain quantitatively the effect of dielectric constant of the medium on the rates of reactions in solutions. Amis and Jaffe [38] predicted a linear relation between  $\log k'$  versus  $1/D$ . The slope of such a plot should be negative for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope obtained for positive ion–dipole reactions. In the present investigations, plots of  $\log k'$  versus  $1/D$  were linear with negative slopes in both cases, thus supporting the participation of the two dipoles in the rate-determining steps (Schemes 2, 4).

#### 4.7 Effect of Ionic Strength

The proposed reaction mechanisms are also evinced by the observed zero effect of ionic strength on the rate of the reaction. The primary salt effect on the reaction rates has been



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 RuCl<sub>3</sub>

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 RuCl<sub>3</sub> 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 RuCl<sub>3</sub>. In the present case,  $x$  value for the standard run was found to be 0.48 for RuCl<sub>3</sub> 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 RuCl<sub>3</sub> catalyst were evaluated. All these results are tabulated in Table 3.

#### 4.9 Comparison of RuCl<sub>3</sub> Catalyzed and Uncatalyzed Reactions

RuCl<sub>3</sub> catalyzed oxidative decolorization of the dye by CAB with that of uncatalyzed reaction (without RuCl<sub>3</sub> catalyst) under an identical set of experimental conditions was compared. The observed rates of oxidative decolorization of the dye in the presence of RuCl<sub>3</sub> 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 RuCl<sub>3</sub> and the oxidant, which increases the oxidizing property of the oxidant than without RuCl<sub>3</sub> catalyst. Further, RuCl<sub>3</sub> 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 RuCl<sub>3</sub> 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 RuCl<sub>3</sub> 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. RuCl<sub>3</sub> 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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