

Dynamic Impact of RuCl₃ Catalyst on the Oxidation of Cyclamate with Acidified Bromamine-T: Elucidation of Mechanistic Pathways and Kinetic Modeling

Ramya Radhakrishnan¹ · Puttaswamy¹

Received: 11 January 2017 / Accepted: 8 March 2017 / Published online: 7 April 2017 © Springer Science+Business Media New York 2017

Abstract Oxidation-Kinetics of cyclamate by bromamine-T (BAT) in $HClO_4$ medium catalyzed by $RuCl_3$ exhibits a first-order dependence on $[BAT]_0$, fractionalorder on both [Cyclamate]₀ and [RuCl₃], and inverse fractional-order on $[HClO_4]$. RuCl₃ catalyst accelerated the reaction by a splendid 48 times. Plausible mechanism and related rate law have been deduced.

Graphical Abstract The Stoichiometry of the reaction is:



(here $Ts = CH_3C_6H_4SO_2$ -)

Puttaswamy pswamy_chem@yahoo.com

1 Introduction

Cyclamate, chemically known as *N*-cyclohexylsulfamic acid, is an artificial sweetener and is used as a non-nutritive sweetener in many dietary and pharmaceutical products [1]. Its potency as a sweetener is around 30 times greater than that of sucrose. On account of its dietary and pharmaceutical potentiality, some of the analytical techniques for the determination of cyclamate including UV spectroscopy [2], chromatography [3], automated turbidimetric technique [4] and flow injection

¹ Department of Chemistry, Bangalore University, Central College Campus, Bangalore 560 001, India

spectrophotometry [5] have been developed. But, to the best of our knowledge there is no report available in the literature about oxidation of cyclamate by any oxidants from its kinetic and mechanistic standpoint. Also, none have examined the impact of platinum metal ions in the oxidation of cyclamate. In view of the significance of this substrate, it is very essential to know its oxidative behaviour towards a +1 oxidant kinetically.

Aromatic N-halosulfonamides or organic N-haloamines are mild oxidants containing strongly polarized N-linked halogen in its +1 oxidation state [6]. Considerable attention has centred on the chemistry of N-haloamines because of their diverse properties to act as halonium cations, hypohalites and N-anions, which behave both as electrophiles and nucleophiles. The chemistry of these compounds has been reviewed by Campbell and Johnson [6], Banerji et al. [7], Agarwal and Upadhyay [8], Kolaveri et al. [9], and Jagadeesh and Puttaswamy [10]. The prominent members of this class of compounds are chloramine-T (p-Me-C₆H₄SO₂NClNa·3H₂O or CAT) and chloramine-B $(C_6H_4SO_2NCINa\cdot 1.5H_2O \text{ or } CAB)$. These reagents have been widely employed as oxidizing agents in the kinetic and mechanistic studies of oxidation of different functional groups in acidic and alkaline medium [7–11]. Bromamine-T (p-Me-C₆H₄SO₂NBrNa·3H₂O or BAT) is the bromine analogue of CAT. Although BAT is found to be a better oxidizing agent than CAT and CAB, only sporadic information exists in the literature on BAT reactions [12–15].

Several preliminary reactions were carried out in our laboratory to oxidize cyclamate under different experimental conditions. The reactions studied using CAT as the oxidant in acid and alkaline media were found to be extremely slow with reaction rates of 1.88×10^{-8} and 1.243×10^{-8} s⁻¹, respectively. So, the choice of CAT as an oxidant was considered inappropriate and was instead replaced by the benzene analogue of CAT, chloramine-B (CAB). The reaction rates observed were not greatly satisfactory, the rate constants being 9.45×10^{-8} and 7.36×10^{-8} s⁻¹ in acidic and basic media, respectively. The use of BAT, the bromine analogue of CAT, as an oxidant stemmed from the earlier discussions. The reaction rates on employing BAT as an oxidant were faster and were found to be 5.12×10^{-6} and 8.31×10^{-7} s⁻¹ in acid and alkaline media, respectively. The reaction in alkaline medium was found to be slow in comparison to the one in acidic medium. All these reactions carried out in CAT, CAB and BAT in acidic and basic media were under similar experimental conditions. The reaction rates discussed proves varied efficiencies of *N*-haloamines as oxidants in the order: BAT>CAB>CAT. In the background of the above facts, it was apt to use BAT as an oxidant in HClO₄ medium to oxidize cyclamate. However, in fact that BAT is a better oxidizing agent in the present study; the reaction is still slow to be studied kinetically to clarify the mechanistic picture of this redox system. Consequently, we thought of using platinum group metal ions as a catalyst to facile the rate of reaction for further kinetic analysis.

The catalysis by platinum metal ions in the redox reactions is of great interest due to strong catalytic influence of these ions in many reactions [16-22]. This catalysis plays an important role in understanding the mechanism of redox reactions. Among the platinum group metal ions, RuCl₃ has widely been used as a homogeneous catalyst in various redox systems [16-22]. This catalysis involves different degrees of complexity, due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium [23, 24]. Literature survey also indicated that no one has examined the role of RuCl₂ or any other platinum metal ions as catalyst in the oxidation of cyclamate. Consequently, the authors employed a trace amount of RuCl₃ catalyst for the oxidation of cyclamate with BAT in acid medium. Surprisingly, it was observed that the slow reaction underwent 48-times faster in the presence of trace amount of RuCl₃(Ca. 8.00×10^{-5} mol dm⁻³). This provoked us to choose RuCl₂ as a catalyst in the present case. In view of the above reasons, we have sought to study the oxidation of cyclamate with BAT in acid medium catalyzed by RuCl₃ in order to unfold the mechanistic picture and catalytic impact of RuCl₃ on this redox system through kinetic study.

On this backdrop, herein we report for the first time the oxidation-kinetics of cyclamate with BAT in acid medium, catalyzed by RuCl₃ in order to throw some light on the mechanistic and catalytic chemistry of this redox system. The objectives of the present investigation are to: (i) develop conditions for the facile oxidation of cyclamate, (ii) examine the influence of reaction parameters on the rate, (iii) elucidate the plausible mechanism, (iv) deduce appropriate rate law, (v) identify the stoichiometry and oxidation products, (vi) ascertain the various reactive species, (vii) find the catalytic efficiency of RuCl₃ on this redox system (viii) demonstrate the formation of complexes, and (ix) evaluate the activation parameters.

2 Experimental

2.1 Materials

The oxidant, BAT, was prepared by the partial debromination of dibromamine-T (DBT) by the standard procedure [25]. An aqueous solution of BAT was prepared afresh, standardized by iodometric method and presereved in brown bottles to prevent its photochemical deterioration. The substrate, sodium cyclamate was obtained from Tokyo Chemical Industry Co., Ltd. Tokyo, Japan and was used as received. An aqueous solution of desired strength of sodium cyclamate was prepared freshly as and when required. Ruthenium trichloride (Merck) solution was prepared in 20 mM HCl solution. Allowance for the amount of acid present in the catalyst solution was made while preparing the reaction mixture for kinetic runs. The addition of methanol in varying proportions (0–30% v/v) was devised to alter the permittivity of the reaction mixture. All chemicals and reagents used in the study were of analytical reagent grade. Aqueous solutions were prepared using double distilled water. UV–Vis SL159 Scanning Spectrophotometer was used for studying the formation of intermediate complexes. Regression coefficients (\mathbb{R}^2) calculations were performed on an f_x -100W scientific calculator.

2.2 Kinetic Measurements

The kinetic procedure followed to study the progress of the reaction was according to a literature procedure [26]. All the kinetic measurements were carried out under pseudo-first-order conditions of $[Cyclamate]_0 >> [BAT]_0$. The kinetic runs were performed in glass stoppered Pyrex boiling tubes coated black from the outside in order to eliminate any possibility of photochemical effects. Reaction mixtures containing requisite amounts of cyclamate, HClO₄ and RuCl₃ were pre-equilibrated at 313 K by placing the tube in a water bath set at the required temperature. The total volume of the solution was maintained constant for all the runs by the addition of adequate quantities of water (50 ml each). To this solution a measured amount of pre-equilibrated (313 K) BAT solution was added to initiate the reaction. The reaction mixture was periodically shaken in order to attain uniform concentration. The progress of the reaction was monitored by iodometric determination of unreacted BAT in 5 ml aliquots of the reaction mixture



Fig. 1 GC-Mass spectrum of cyclohexanone with its molecular ion peak at 98 amu

at regular intervals of time. The course of the reaction was studied for more than two half-lives. The pseudo-first-order rate constants ($k' \, s^{-1}$) calculated from the linear plots of log [BAT] versus time were reproducible within 3–5%. k' values reported are the mean values of duplicate kinetic runs.

3 Results

3.1 Stoichiometry

Reaction mixtures constituting varying ratios of cyclamate and BAT in presence of 1.00×10^{-3} mol dm⁻³ HClO₄ and 8.00×10^{-5} mol dm⁻³ RuCl₃ were equilibrated at 313 K for 24 h with occasional stirring. The iodometric titration of unreacted BAT in the reaction mixture showed that 1 mol of BAT was consumed per mole of cyclamate. The observed stoichiometric results could be represented in the form of the equation given below:

$$\begin{array}{c} & O \\ + \text{ TsNHBrNa} + H_2O \end{array} \rightarrow \begin{array}{c} O \\ + \text{ NH}_2SO_3H + \\ & \text{TsNH}_2 + Na + Br \end{array}$$
(1)

(here $T_s = CH_3C_6H_4SO_2 -)$.

3.2 Product Analysis

The reaction mixtures as per the stoichiometric ratio arrived at were again made to react for 24 h at 313 K under stirred conditions. On completion of the reaction (monitored by TLC), the mixture was neutralized by NaOH and the reaction products were extracted with ether. An oily liquid (cyclohexanone) was obtained on drying the organic layer, whereas the aqueous layer furnished a solid (sulfamic acid) on drying. Cyclohexanone was characterized by GC-MS data, which showed a molecular ion peak at 98 amu (Fig. 1). Following which the solid obtained on drying the aqueous layer was subjected to column chromatography on silica gel (60-200 mesh) using gradient elution from dichloromethane to chloroform. After initial separation the products were further purified by recrystallization. The other product of cyclamate oxidation sulfamic acid, was identified [27] by the reaction of product with nitrous acid which converted the former to sulfuric acid, this on reaction with barium chloride formed a white precipitate of barium sulfate. The reduction product of BAT, p-toluenesulfonamide (PTS) was extracted with ethyl acetate and detected by paper chromatography [28]. Benzyl alcohol saturated with water was used as solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent ($R_f = 0.905$). PTS was further ascertained by GC-MS analysis with the



Fig. 2 GC-Mass spectrum of *p*-toluenesulfonamide with its molecular ion peak at 171 amu

molecular ion peak at 171 amu (Fig. 2) and also from the melting point value of 138 °C (lit mp 138–139 °C). It was noticed that there was no further oxidation of these products under the prevailing kinetic conditions.

The oxidation products cyclohexanone and sulfamic acid, both of which find extensive industrial applications [29, 30]. A major part of the world's supply of cyclohexanone is converted to adipic acid and cyclohexanone oxime, the former is one of the precursors for Nylon 6,6. A major reactant in the manufacture of Nylon 6 is caprolactum, which is in turn obtained from cyclohexanone. It is also used as a solvent for cellulose lacquers. The byproduct sulfamic acid is used in the design of many drugs including anti-cancer, anti-epileptic, weight loss drugs etc apart from being used as a cleansing reagent in industries. Hence, the present reaction is an important protocol in synthetic chemistry.

3.3 Effect of Varying BAT and Cyclamate Concentrations on the Rate of Reaction

Under the pseudo-first-order conditions $([Cyclamate]_0 >> [BAT]_0)$, maintaining the concentrations of $[Cyclamate]_0$, $[RuCl_3]$, $[HClO_4]$ and the temperature to be constant, plots of log [BAT] versus time were found to be linear ($\mathbb{R}^2 > 0.9975$) for varying $[BAT]_0$, indicates a first-order dependence of oxidant on the rate of reaction. Further k' was not affected by a change in $[BAT]_0$, confirming the first-order dependence of rate on $[BAT]_0$. The pseudo-first-order rate constants obtained

Table 1 Effect of varying oxidant, substrate, acid and catalyst concentrations on the rate of reaction at 313 K

$10^4 [BAT]_0$ (mol dm ⁻³)	10^{3} [cyclamate] ₀ (mol dm ⁻³)	$10^3 [HClO_4]$ (mol dm ⁻³)	$10^{5} [RuCl_{3}]$ (mol dm ⁻³)	$10^4 k' (s^{-1})$
0.5	5.0	1.0	8.0	2.39
0.75	5.0	1.0	8.0	2.36
1.0	5.0	1.0	8.0	2.49
2.5	5.0	1.0	8.0	2.30
5.0	5.0	1.0	8.0	2.33
1.0	1.2	1.0	8.0	1.47
1.0	2.0	1.0	8.0	2.02
1.0	5.0	1.0	8.0	2.49
1.0	7.0	1.0	8.0	4.72
1.0	10.0	1.0	8.0	5.20
1.0	5.0	0.5	8.0	3.26
1.0	5.0	0.75	8.0	2.46
1.0	5.0	1.0	8.0	2.49
1.0	5.0	2.0	8.0	1.77
1.0	5.0	4.0	8.0	0.97
1.0	5.0	1.0	2.5	1.61
1.0	5.0	1.0	5.0	1.86
1.0	5.0	1.0	8.0	2.49
1.0	5.0	1.0	11.0	2.92
1.0	5.0	1.0	13.0	2.95

are listed in Table 1. Under the prevailing experimental conditions, an increase in $[Cyclamate]_0$ was found to increase the rate of the reaction (Table 1). A plot of log k' versus log $[Cyclamate]_0$ was found to be linear $(R^2=0.9956)$ with a slope of 0.28, which stems from the fact that there is a fractional-order dependence on $[Cyclamate]_0$. Further, a plot of k' versus $[Cyclamate]_0$ was linear $(R^2=0.9956)$ with a y-intercept which confirmed a fractional-order dependence of rate on $[Cyclamate]_0$.

3.4 Effect of Varying HClO₄ and RuCl₃ Concentrations on the Rate of Reaction

The influence of [HClO₄] on the reaction rate was determined by varying [HClO₄] under the prevailing conditions of the reaction (Table 1). There was a retarding influence on the rate of the reaction as the [HClO₄] was increased. The log–log plot of k' versus [HClO₄] was linear (R²=0.9769) and possessed an order of -0.57, indicating a negative-fractional-order dependence of rate on [HClO₄]. An increase in [RuCl₃] was found to enhance the rate of reaction (Table 1). A plot of log k' versus log [RuCl₃] was linear (R²=0.9821) with a slope of 0.30, **Table 2** Effect of varying die-lectric constant of the mediumon the rate of reaction at 313 K

% MeOH v/v)	D	$10^4 k' ({ m s}^{-1})$
)	76.73	2.49
10	72.37	2.24
20	67.48	2.06
30	62.71	1.77

 $[BAT]_0=1.0\times10^{-4} \text{ mol } dm^{-3};$ $[cyclamate]_0=5.0\times10^{-3}$ $mol dm^{-3}; [HClO_4]=1.0$ $\times10^{-3} mol dm^{-3}; [RuCl_3]=$ $8.0\times10^{-5} mol dm^{-3}$

indicating a fractional-order dependence on the rate of the reaction.

3.5 Effect of Varying Halide Ions Concentrations on the Rate of Reaction

The addition of Cl⁻ or Br⁻ ions in the form of NaCl or NaBr solution $(4.0 \times 10^{-3} \text{ mol dm}^{-3})$ proved ineffective in bringing about any significant change on the rate of the reaction. This enabled to conclude that the Cl⁻ or Br⁻ ions do not play any role in the reaction.

3.6 Effect of Varying PTS Concentration on the Rate of Reaction

p-Toluenesulfonamide (PTS), the reduction product of BAT, was added to the reaction mixture $(6.0 \times 10^{-3} \text{ mol dm}^{-3})$ which left the rate of reaction significantly unaltered. This was evidence to show that PTS is not involved in any step prior to the rate-determining step (rds) in the proposed scheme.

3.7 Effect of Varying Ionic Strength of the Medium on the Rate of Reaction

Keeping all the other experimental conditions constant, the effect of ionic strength on the rate of reaction was studied by adding 0.30 mol dm^{-3} NaClO₄ solution in to the reaction mixture. The rate of reaction was not altered significantly. Hence, no efforts were made to keep the ionic strength of the medium constant for kinetic runs.

3.8 Effect of Varying Dielectric Constant of the Medium on the Rate of Reaction

Kinetic studies were carried out in H_2O –MeOH mixtures of varying compositions (0–30% v/v), thereby changing the dielectric constant of the solvent medium. The rate was found to decrease with increase in MeOH content and a plot of log k' versus 1/D was linear ($R^2=0.9953$) with a negative slope. The results are reported in Table 2 and graphically represented in Fig. 3. The values of dielectric constant of H₂O–MeOH mixture as reported in the literature [31] were employed. Blank experiments were performed to ensure that there was no oxidation of MeOH by BAT, under the prevailing experimental conditions.

3.9 Effect of Varying Temperature on the Rate of Reaction

The reaction was studied at five different temperatures (303, 308, 313, 318 and 323 K) in the presence and absence of RuCl₃ catalyst, maintaining other experimental conditions constant. From the linear Arrhenius plot of log k' versus 1/T (Fig. 4; R²=0.9856), the values of activation parameters (E_a, $\Delta H^{\#}$, $\Delta G^{\#}$, $\Delta S^{\#}$) were evaluated. All these results are tabulated in Table 3.

3.10 Polymerization Study

The addition of reaction mixtures to aqueous acrylamide monomer solutions, kept in dark, was unable to initiate polymerization. It proves the absence of any free radical species generated during reaction. The control experiments were carried out under similar reaction conditions without the oxidant.

4 Discussion

4.1 Reactive Species

Irrespective of whether the medium is acidic or basic, *N*-haloamines have been proved to be mild oxidants [7]. *N*-haloamines are compounds containing halonium cations; the presence of only one halogen brings about an efficient two-electron transfer in their reactions. Bromamine-T, like its chlorine analogue chloramine-T, behaves as a strong electrolyte in aqueous solutions and depending on its pH, it furnishes different types of reactive species [32–34].

The possible oxidizing species in acid medium are the free acid (TsNHBr), DBT (TsNBr₂), HOBr and H₂O⁺Br. Hence, in acidified solution of BAT there are four possible species which can oxidize the substrate. From these four possibilities, the active reactive species of BAT can be decided based on observed kinetic results. If TsNBr₂ was involved in the reaction mechanism, it would have led to a second-order dependence of rate on [BAT]₀ and also an inverse effect of TsNH₂ (PTS) on the rate. But both of



Fig. 3 plot of $\log k'$ versus 1/D



Fig. 4 Plot of log k' versus 1/T

these contradict the experimental observations. Whereas, if HOBr were the primary oxidizing species, the addition of TsNH₂ to the reaction medium should have caused a decrease in the rate of reaction; but the experimental evidence obtained stands against this expectation by leaving the reaction rate unaffected. Studies pertaining to pH-dependent relative concentrations of acidified haloamine solutions bearing comparable concentrations have shown the possibility of free acid being the most likely oxidizing species [34]. Furthermore, the formation of the diprotonated species (TsN⁺H₂Cl) with a protonation constant of 1.02×10^{-2} M⁻¹ at pH 2 has been reported for CAT in acid solutions [35, 36].

$$TsNHCl + H^+ \rightleftharpoons TsN^+H_2Cl$$
(2)

Table 3 Effect of varying temperature on the rate of reaction and values of activation parameters for the oxidation of cyclamate by BAT in acid medium in the presence and absence of RuCl₃ catalyst

Temperature (K)	$10^6 k' (s^{-1})$ Uncatalyzed	$10^4 k' (s^{-1})$ RuCl ₃ catalyzed	$10^3 K_c$
303	2.47	1.36	2.26
308	3.37	1.54	2.54
313	5.11	2.49	4.14
318	6.21	3.84	6.39
323	9.59	4.99	8.29
E _a (kJ mol ⁻¹)	53.9	35.1	54.7
$\Delta H^{\#} (kJ mol^{-1})$	51.3 ± 0.01	32.5 ± 0.01	52.1 ± 0.01
$\Delta G^{\#} (kJ mol^{-1})$	108 ± 0.31	98.4 ± 0.24	91.1 ± 0.20
$\Delta S^{\#} (JK^{-1} \; mol^{-1})$	-183 ± 0.12	-210 ± 0.36	-124 ± 0.25

 $[BAT]_0 = 1.0 \times 10^{-4} \text{ mol } dm^{-3}; [cyclamate]_0 = 5.0 \times 10^{-3} \text{ mol } dm^{-3}; [HCIO_4] = 1.0 \times 10^{-3} \text{ mol } dm^{-3}; [RuCl_3] = 8.0 \times 10^{-5} \text{ mol } dm^{-3}$

Values at the last row are the catalytic constants (K_c) at different temperatures and activation parameters with respect to ${\rm RuCl}_3$ catalyst

Since organic *N*-haloamines express similar chemical behaviours, the above equilibrium can be applied to BAT as well. If the diprotonated species is taken as the reactive species of BAT it will lead to a positive effect of $[H^+]$ on the rate of oxidation, which is contrary to the observed negative effect of $[H^+]$ on the rate. Hence, in the present case a fractional negative-order dependence on $[H^+]$ suggests the backward reaction as represented by Eq. (2) to be feasible. This implies that in the present case TsNHBr is the reactive oxidizing species involved in the oxidation of cyclamate.

Electronic spectral studies carried out by Cady and Connick [37], and Connick and Fine [38] reveal that species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2-}$ are absent in an aqueous solution of RuCl₃. A detailed study [39, 40] on the possible oxidation states of RuCl₃ in aqueous acidic medium has revealed the following equations:

$$\operatorname{RuCl}_{3} \cdot x\operatorname{H}_{2}\operatorname{O} + 3\operatorname{HCl} \rightleftharpoons \left[\operatorname{RuCl}_{6}\right]^{3-} + x\operatorname{H}_{2}\operatorname{O} + \operatorname{H}^{+} \qquad (3)$$

$$\left[\operatorname{RuCl}_{6}\right]^{3-} + \operatorname{H}_{2}O \rightleftharpoons \left[\operatorname{RuCl}_{5}(\operatorname{H}_{2}O)\right]^{2-} + \operatorname{Cl}^{-}$$
(4)

In the present study the addition of Cl⁻ ions fails to bring about any significant change on the rate of reaction, indicating that the equilibrium represented by Eq. (4) does not contribute greatly in the reaction. Hence, the complex ion $[RuCl_5(H_2O)]^{2-}$ is assumed to be the reactive catalytic species that interacts with BAT to form an intermediate complex.

4.2 Reaction Scheme

In the light of the above facts, Scheme 1 is put forward for the RuCl₃ catalyzed oxidation of cyclamate by BAT in acid medium to substantiate the experimental observations. A detailed mechanistic interpretation of RuCl₃ catalyzed BAT-cyclamate redox reaction in HClO₄ medium is illustrated in Scheme 1. According to Scheme 1, step (i) involves a fast deprotonation of TsN⁺H₂Br leading to the formation of the active oxidant species TsNHBr in the acid retarding step. Following this, the active catalyst RuCl₃ forms a partial bond with the nitrogen of TsNHBr, which yields Complex-I (step (ii)) along with elimination of a molecule of water. An attack of the substrate cyclamate, on Complex-I occurs by the breakage of an $N-S\pi$ bond of the former, leading to the formation of Complex-II (step (iii)). Following this fast equilibrium step, Complex-II, through a slow and rds (step (iv)) undergoes deprotonation resulting in the formation of Complex-III with the simultaneous elimination of PTS and [RuCl₅H₂O]²⁻. A nucleophilic attack on the electrophilic nitrogen centre of Complex-III by a molecule of water may yield the ultimate products cyclohexanone and sulfamic acid as shown in the Scheme 1 (step (v)).

4.3 Spectroscopic Evidence for Complex Formation

The evidence required to prove the formation of Complex-I between oxidant and catalyst species (step (ii) of Scheme 1) were obtained from the UV-Vis spectra of BAT, RuCl₃ and (BAT+RuCl₃) mixture. Absorbance maxima in acid medium were observed at 227.1 and 361.8 nm respectively for BAT and $RuCl_3$ whereas in (BAT + $RuCl_3$) mixture it was observed at 342.8 nm which is a hypsochromic shift of 19 nm as expected from the structure of Complex-I. These are illustrated in the Fig. 5. Further evidence for the formation of Complex-II has been evinced from the UV-Vis absorbance maxima at 331.6 nm of $(BAT + RuCl_3 + Cycla$ mate) mixture where the UV inactive cyclamate brings about a hypsochromic shift of 11.2 nm in the absorbance maxima of $(RuCl_3 + BAT)$ as in Fig. 5. The wavelengths obtained from the previous data were now found to further shift lower, thus proving this complex to be unstable.

4.4 Deduction of Rate Law

The rate law for Scheme 1 can be deduced as follows: The total effective concentration of BAT is:

 $[BAT]_{t} = \left[Ts \overset{+}{N}H_{2}Br\right] + [TsNHBr] + [Complex - I] + [Complex - II]$

(5)



Scheme 1 A detailed mechanistic description for RuCl₃ catalyzed oxidation of cyclamate by BAT in acid medium

From steps (i), (ii) and (iii) of Scheme 1, the values of $[TsN^+H_2Br]$, [TsNHBr] and [Complex-I] were found to be:

$$\begin{bmatrix} \operatorname{Ts} \overset{+}{\mathrm{N}} \operatorname{H}_{2} \operatorname{Br} \end{bmatrix} = \frac{\begin{bmatrix} \operatorname{Complex} - \operatorname{II} \end{bmatrix} \begin{bmatrix} + \\ \mathrm{H} \end{bmatrix}}{\operatorname{K}_{1} \operatorname{K}_{2} \operatorname{K}_{3} \begin{bmatrix} \operatorname{Cyclamate} \end{bmatrix} \begin{bmatrix} \operatorname{RuCl}_{3} \end{bmatrix}}$$
(6)

$$[TsNHBr] = \frac{[Complex - II]}{K_2 K_3 [Cyclamate] [RuCl_3]}$$
(7)

$$[\text{Complex - I}] = \frac{[\text{Complex - II}]}{\text{K}_3[\text{Cyclamate}]}$$
(8)



Fig. 5 UV–Vis spectra of a $RuCl_3$, b $RuCl_3$ +BAT+Cyclamate, c $RuCl_3$ +BAT, d BAT

By substituting for $[TsN^+H_2Br]$, [TsNHBr] and [Complex-I] from Eqs. (6), (7) and (8) in Eq. (5), the value of [Complex-II] was obtained as:

From the value of intercept, the decomposition constant (k_4) could be derived as $8.33 \times 10^{-4} \text{ s}^{-1}$.

Scheme 1 and rate law (11) can explain the following observed experimental results:

4.5 Effect of Dielectric Constant

Since, most of the organic reactions require a medium to make the reaction feasible, it is apt to use solvents of varying nature; the effects of these on the rate should thus be assessed. This can be achieved by changing the solvent composition by varying the methanol content in the reaction mixture [41–44]. For limiting case of zero angle approach between two dipoles or an ion dipole system, Amis [44] has shown that a plot of log k' versus 1/D gives a straight line, with a positive slope for a reaction involving a positive ion and a dipole, and a negative slope for a negative ion–dipole or dipole–dipole interactions. In the present investigations, a plot of log k' versus 1/D was linear with a negative slope. The observation can be thus directed towards a negative ion–dipole interaction as observed in the rate-determining step (Scheme 1. step

$$\left[\text{Complex - II}\right] = \frac{K_1 K_2 K_3 [\text{BAT}]_t [\text{RuCl}_3] [\text{Cyclamate}]}{K_3 [\text{H}^+] + K_1 + K_1 K_2 [\text{RuCl}_3] + K_1 K_2 K_3 [\text{RuCl}_3] [\text{Cyclamate}]}$$
(9)

From the slow and rds (step (iv)) of Scheme 1,

 $Rate = k_4 [Complex - II]$ (10)

On substitution of [Complex-II] from Eq. (9) in Eq. (10), the rate law is given as,

$$Rate = \frac{K_1 K_2 K_3 k_4 [BAT]_t [RuCl_3] [Cyclamate]}{[H^+] + K_1 + K_1 K_2 [RuCl_3] + K_1 K_2 K_3 [RuCl_3] [Cyclamate]}$$
(11)

Rate law (11) predicts a first-order dependence of reaction rate on $[BAT]_0$, fractional order on both $[Cyclamate]_0$ and $[RuCl_3]$ and an inverse-fractional-order with respect to $[H^+]$, in agreement with our experimental results.

Since rate = $k'[BAT]_t$, then

$$k' = \frac{K_1 K_2 K_3 k_4 [RuCl_3] [Cyclamate]}{[H^+] + K_1 + K_1 K_2 [RuCl_3] + K_1 K_2 K_3 [RuCl_3] [Cyclamate]}$$
(12)

Equation (12) can be transformed as,

(iv)), wherein anionic Complex-II reacts with a molecule of water.

4.6 Effect of Ionic Strength

The ionic strength of the solution as well as the charges borne by the reactive species has a pronounced effect on the rate of ionic reactions. The study of the influence of ionic strength on the rate of reaction gives valuable information about the type of the species involved in the rate-determining step, i.e. whether they are ionic or non-ionic in nature [45]. The effect of primary salt on the reaction is explained by Bronsted and Bjerrum equation:

$$\log k' = \log k_0 + 1.018 Z_A Z_B \sqrt{I}$$
(14)

Here *I* is the ionic strength of the reaction medium: k' and k_0 , the specific rate constants in the bulk of the reaction and infinite dilution; and Z_A and Z_B , the ionic charges of the reac-

$$1/k' = \frac{1}{[\text{Cyclamate}]} \left\{ \frac{[\text{H}^+]}{\text{K}_1 \text{K}_2 \text{K}_3 \text{k}_4 [\text{RuCl}_3]} + \frac{1}{\text{K}_2 \text{K}_3 \text{k}_4 [\text{RuCl}_3]} + \frac{1}{\text{K}_3 \text{k}_4} \right\} + \frac{1}{\text{k}_4}$$
(13)

Based on Eq. (13), a plot of 1/k' versus 1/[Cyclamate] should be linear as it is actually found ($R^2 = 0.9945$).

tants A and B. The variation in k' with ionic strength should depend on the sign of Z_A and Z_B . From the above equation,

a plot of log k' versus square root of *I* would be linear yielding a slope equal to $1.018Z_AZ_B$ and an intercept log k₀. This equation predicts that (i) if both ions have same charges, then Z_AZ_B is positive and so k' increases with I; (ii) if Z_A and Z_B have opposite signs, then Z_AZ_B is negative and so k' decreases with I; and (iii) if either Z_A or Z_B bears no charge on it, then Z_AZ_B is zero, so k' is independent of the ionic strength of the solution. In the present investigations, variation in ionic strength of medium by adding 0.30 mol dm⁻³ NaClO₄ solution left the reaction rate unaltered. This can be explained by the species involved in the rate determining step, wherein Complex (II) is negatively charged and the water molecules in the medium are neutral (step (iv) of Scheme 1). Therefore, the observed ionic strength effect is in accordance with the Bronsted-Bjerrum concept [45] and proposed scheme.

4.7 Catalytic Activity

Moelwyn-Hughes [46] pointed out that the $RuCl_3$ catalyzed and uncatalyzed reactions proceed in a parallel way abiding by the equation:

$$\mathbf{k}_1 = \mathbf{k}_0 + \mathbf{K}_c \left| \text{catalyst} \right|^{\wedge} \tag{15}$$

Here k_1 is the observed pseudo-first-order rate constant obtained in the presence of RuCl₃ catalyst and k_0 is that for the uncatalyzed reaction (in the absence of RuCl₃ catalyst) K_c is the catalytic constant and x is the order of the reaction with respect to RuCl₃, which is found to be 0.30 in the present investigations. The values of the catalytic constants K_c at five different temperatures 303, 308, 313, 318 and 323 K were calculated using the relationship:

$$\mathbf{K}_{c} = \left(\mathbf{k}_{1} - \mathbf{k}_{0}\right) / \left[\mathbf{Ru}(\mathbf{III})\right]^{x}$$
(16)

The values of K_c were found to alter with change in temperature. A linear plot of log K_c versus 1/T ($R^2=0.9851$) was employed to evaluate the activation parameters with respect to RuCl₃. The results of which are tabulated in Table 3.

4.8 Comparison of RuCl₃ Catalyzed and Uncatalyzed Reactions

According to rate constants reported in Table 3, it can be seen that oxidation of RuCl_3 catalyzed reaction is 48-fold faster than the uncatalyzed reaction. This justifies the need of RuCl_3 as a catalyst in the oxidation of cyclamate using BAT in acid medium, which otherwise as observed the reaction was found to be extremely sluggish to be studied kinetically. Complex-I is formed between the catalyst and oxidizing species, which increases the efficiency of oxidation in comparison to that in the absence of the former. This complex aids the attack on the substrate resulting in the catalyst providing an alternate reaction path by affording a lower activation energy barrier (Table 3) for the reactants to cross over it and enabling the reaction to be relatively facile.

4.9 Activation Parameters

The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The transition state can be predicted to be in a highly solvated state from the positive $\Delta H^{\#}$ and $\Delta G^{\#}$ values obtained. The large negative entropy of activation may be interpreted as due to a fraction of collisions which become more stringent and form a rigid associative complex, resulting in a slow decomposition of the Complex (II). The rate of the reaction remains to be irresponsive to the addition of *p*-toluenesulfonamide which is in turn justified by the species appearing only in the rate-determining step and not prior to it. The addition of bromide ions also proved to be ineffective on the rate of the reaction, which is in agreement with the fact that bromide ions are not involved in the reaction mechanism. Thus, the proposed mechanism as well as the derived rate law is in complete agreement with all experimental findings.

5 Conclusion

The kinetics of oxidation of cyclamate with BAT in acid medium catalyzed by RuCl₃ obeys the experimental rate law: $-d[BAT]/dt = k [BAT]_0 [cyclamate]_0^x [H^+]^{-y} [RuCl_3]^z$ here x, y and z are found to be 0.28, -0.57 and 0.30 respectively. Cyclohexanone and sulfamic acid were identified as the oxidation products of cyclamate. Overall activation parameters and also with respect to RuCl₃ catalyst have been deduced. The RuCl₃ catalyzed reaction was found to be 48-fold faster than the uncatalyzed reaction. This justifies the use of RuCl₃ catalyst for cyclamate-BAT redox system in acid medium. TsNHBr and $[RuCl_5(H_2O)]^{2-}$ are found to be the reactive species of oxidant and catalyst, respectively. Spectroscopic evidence for the formation of complexes between oxidant, catalyst and substrate has been provided. The best fitted mechanism and rate law based on the kinetic results have been arrived at.

Acknowledgements We gratefully acknowledge Professor M. A. Pasha, Department of Chemistry, Bangalore University, Bangalore for his helpful discussions about the Scheme 1.

References

 Steve M (2003) Biological interactions of sulphur compound. CRC Press, Boca Raton

- 2. HU ML, Tsai HH (1998) Food Chem Toxicol 36:755-759
- Isidre C, Maria R, Judith A, Margarita F, Lluis SM (1996) J Chromatography A 750:397–402
- 4. Miriam EP, Beatriz SFB, Natalia EL, Mar´ıa SDiN (2005) Anal Chim Acta 539:301–304
- Carolina C, Javier S, Santiago HC (1999) Analatica Chimica Acta 381(2,3):307–313
- 6. Campbell MM, Johnson G (1978) Chem Rev 78:65
- Banerji KK, Jayaram B, Mahadevappa DS (1987) J Sci Ind Res 46:65
- 8. Agarwal MC, Upadhyay SK (1990) J Sci Ind Res 49:13
- Kolaveri E, Ghorbeni-Choghamarani A, Salehi P, Shirini F, Zolfigol MA (2007) J Iran Chem Soc 4:126–174
- Jagadeesh RV, Puttaswamy (2013) Encyclopedia of reagents for organic synthesis Chloramine-T: second update, RC056, 9
- Aftab APK, Abdullah MA, Anish K, Abdulrahman OA (2012) Ind Eng Res 51(13):4819–4824
- 12. Puttaswamy, Mahadevappa DS, Rangappa KS (1989) Bull Chem Soc Jpn 62:3343
- Puttaswamy, Anuradha TM, Ramachandrappa R, Gowda NMM (2000) Int J Chem Kinet 32(4):221
- 14. Puttaswamy, Jagadeesh RV (2005) Applied Catal A 292:259
- Chandrashekar, Venkatesha BM, Ananda S, Gowda NMM (2013) Mod Res Catal 2(4):157
- 16. Bhat KR, Jyothi K, Gowda BT (2002) Oxid Commun 25:117
- 17. Mulla RM, Hiremath G, Nandibewoor ST (2005) J Chem Sci 117(1):33
- 18. Saxena R, Gupta S, Upadhyay SK (1990) Ind J Chem 29A:840
- 19. Putaswamy, Nirmala V (2001) Stud Surf Sci Catal 133:535
- 20. Jagadeesh RV, Puttaswamy (2008) J Phys Org Chem 21(10):844–858
- 21. Dakshayani S, Puttaswamy (2016) Appl Catal A 513:116
- Aftab APK, Anish K, Abdullah MA, Naved A, Malik AR (2014) J Taiwan Inst Chem Eng 45:127–133
- 23. Griffith WP (1967) The chemistry of rare platinum metals. Interscience, New York
- 24. Cotton FA, Wilkinson G, Murillo CA, Bochmann M (1999) Advanced inorganic chemistry. Wiley, New York
- 25. Nair CGR, Kumari RL, Indrasenan P (1978) Talanta 27:525

- 26. Dakshayani S, Manjunatha AS, Puttaswamy (2016) Catal Lett 146:180
- 27. Anthony GB, William (1980) J Chem Rev 80:151-186
- Vinod KN, Puttaswamy, Gowda KNN (2009) Inorg Chim Acta 362:2044
- Michael TM (2005) Cyclohexanol and cyclohexanone in Ullmann's encyclopedia of industrial chemistry. Wiley VCH, Weinheim
- 30. Leallyn BC (1943) J Chem Educ 20(4)189
- Akerloff G (1932) Dielectric constants of some organic solventswater mixtures at various temperatures. J Chem Soc 54:4125
- Morris JC, Salazar JA, Wineman MA (1948) J Am Chem Soc 70:2036
- Hardy FF, Johnston JP (1973) The Interactions of N-bromo-Nsodiumbenzenesulfonamide(bromamine-B) with p-nitro phenoxide ion. J Chem Soc Perkin Trans II 742–746
- 34. Bishop E, Jennings VJ (1958) Talanta 1:197
- 35. Narayanan SS, Rao VRS (1983) Radiochem Acta 32:211-212
- Subhashini M, Subhramaniam M, Rao VRS (1985) Talanta 32:1082–1085
- 37. Cady HH, Connick RE (1958) J Am Chem Soc 80:2646
- 38. Connick RE, Fine DA (1960) J Am Chem Soc 82:4187
- Backhours JR, Doyer FD, Shales N (1950) Proc Roy Soc 83:146–155
- 40. Davfokratova T (1963) Analytical chemistry of ruthenium. Academy of Sciences, USSR, Moskava
- Frost AA, Pearson RG (1961) Kinetics and mechanism, 2nd edn. Wiley, New York
- 42. Entelis SG, Tiger RP (1976) Reaction kinetics in the liquid phase. Wiley, New York
- Reichardt C (2003) Solvent and solvent effects in organic chemistry, 3rd edn. Wiley, New York
- 44. Amis ES (1966) Solvent effects on reaction rates and mechanism. Academic Press, New York
- 45. Laidler KJ (1987) Chemical kinetics. Pearson educ Inc, New Delhi
- Moelwyn-Hughes EA (1947) Kinetics of reactions in solutions. Oxford University Press, London, pp 297–299