

Kinetics and Mechanistic Studies of Ru(III) Catalyzed Oxidation of *p*-Hydroxy Benzoic Acid by Sodium *N*-chloro-*p*-toluene Sulphonamide in Acidic Media

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Kinetics studies of the oxidation of *p*-hydroxy benzoic acid by sodium *N*-chloro-*p*-toluene sulphonamide (chloramine-T or CAT) have been carried out in aqueous perchloric acid medium at 35 °C. The reaction follows almost similar kinetics, being first order with respect to chloramine-T, *p*-hydroxy benzoic acid and Ru(III). The reaction exhibits inverse first order dependence on the concentration of medium [HClO₄]. Variation of ionic strength by adding NaClO₄ have no significant effect on the reaction rate. The addition of *p*-toluene sulphonamide, which is one of the reaction products, had no significant effect on the reaction rate. Thermodynamic parameters were computed by studying the reactions at different temperature (303-318 K). The rate laws derived are in excellent agreement with the experimental results. A mechanism consistent with the above kinetic result has been suggested.

Keywords: Kinetics, Mechanism, *p*-Hydroxy benzoic acid, Chloramine-T, Oxidation, Perchloric acid, Ruthenium(III) chloride.

INTRODUCTION

The chemistry of aromatic sulphonyl haloamines has evoked considerable interest as they act as sources of halonium cations, hypohalite species and N-anions which act both as bases and nucleophiles¹. The prominent members of this group are chloramine-T [CAT] and chloramine-B [CAB] and the mechanistic aspects of many of these reactions have been explained². Chloramine-T [CAT] is a strong electrolyte stable in aqueous solution and has been extensively used as an oxidant and synthetic reagent³. Chloramine-T acts as an oxidizing agent in both acidic and alkaline media^{4,5}. The redox potential^{6,7} of chloramine-T/RNH₂ (where RNH₂, the reduction product of chloramine-T is *p*-toluene sulphonamide) is pH dependent and decreases with increases in pH of the medium. Generally, chloramine-T (CAT or RNCINa, where R = CH₃C₆H₄SO₂) undergoes a two electron change in its reaction. Depending on pH of the medium, CAT furnishes different types of reactive species in solution such as RNHCl, RNCl₂, HOCl and possibly H₂OCl⁺ in acid solutions and RNCl⁻ and OCl⁻ ions in alkaline medium⁸.

The potent oxidant is of special interest for studying reaction mechanism as it behaves as both a chlorinating and oxidizing agent⁹. It has been used widely for the quantitative direct and indirect determination of a large number of inorganic and organic compounds¹⁰. Although kinetic species of uncatalysed reaction involving CAT as oxidant¹¹⁻¹⁵ have been

made but few kinetic studies of catalysed CAT oxidations are reported¹⁶⁻²⁰.

Oxidation of *p*-hydroxy benzoic acid is of great importance from a chemical point of view. *p*-Hydroxy benzoic acid is used in the synthesis of dyes and many esters of (*p*-HBA) have antiseptic properties.

The catalysis by transition metal ions in redox reactions is of immense interest²¹ and it plays an important role in understanding the mechanism of redox reactions. Their oxidizing and catalytic properties are due to the existence of variable oxidation states, as a consequence of partly filled *d* or *f* orbitals. Their ability to form both σ and π bonds with other moieties or ligands is one of the chief factors for imparting catalytic properties to transition metals as well as their complexes. Most of the *d*-block elements show characteristic interligand migration reactions and such a process forms one of the most important type of reactions in homogeneous catalysis. Ruthenium(III) chloride has been widely used as a homogeneous catalyst in various redox reactions²². The utility of ruthenium(III) chloride as a non-toxic and homogeneous catalytic has been reported by several workers²³. The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radicals and different oxidizing states of Ru(III).

There are few reports on the kinetics of oxidation of *p*-hydroxy benzoic acid by CAT but least attention has been focused on CAT reaction with *p*-hydroxy benzoic acid

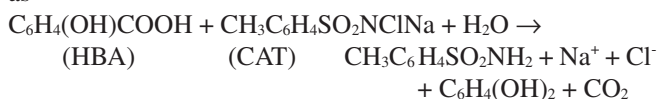
using Ru(III) as catalyst particularly in acidic medium. So, this prompted us to investigate the systematic kinetic study of the oxidation of *p*-hydroxy benzoic acid by ruthenium(III) chloride in acidic medium.

EXPERIMENTAL

The reagents employed were *p*-hydroxy benzoic acid (E. Merck), ruthenium chloride (Johnson & Matthey) and chloramine-T (E. Merck). All other reagents were of A.R. grade. All solutions of the reagents were prepared in doubly distilled water. The prepared solution of chloramine-T was standardized iodometrically. The stock solution of *p*-hydroxy benzoic acid was prepared by dissolving the appropriate amount of it in known volume of distilled water and standardized against the standard solution of sodium hydroxide. In order to prevent any photochemical decomposition, the solution of chloramine-T was stored in black coated bottles. The reaction bottles were also coated black from outside to avoid any photochemical effect. Perchloric acid (E. Merck) was used as a source of hydrogen ions and its solution were prepared in doubly distilled water.

Appropriate amounts of reactant were taken in a one vessel blackened outside and in another CAT which thermostated at the desired temperature (± 0.1 °C). The reaction was initiated by rapidly adding a required amount of CAT solution to the reaction mixture. Aliquots (10 mL each) of the reaction mixture were withdrawn at regular time intervals and unconsumed amount of CAT were determined iodometrically, using starch as an indicator. The rate of reaction ($-dc/dt$) in each kinetic run was calculated with the help of the slope of the tangent drawn at fixed [chloramine-T] in the plot of unconsumed [chloramine-T] vs. time. The order of reaction with respect to each reactants was calculated by the relationship between the initial rate ($-dc/dt$) and concentration of each reactants.

Varying ratios of [CAT] and *p*-HBA under the condition of [CAT] \gg [Substrate] were equilibrated at room temperature for 48 h. Estimation of unreacted CAT, showed that in the oxidation of *p*-HBA only one mole of chloramine-T was consumed. The observed stoichiometry may be represented as -



where $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ represents *p*-hydroxy benzoic acid while $\text{C}_6\text{H}_4(\text{OH})_2$ represents reaction product as quinol which was detected and estimated gravimetrically as well as by TLC²⁴.

RESULTS AND DISCUSSION

The reaction was studied at several initial concentrations of the reactants and the kinetic results were reported in Table-1. The rate of reaction- dc/dt increases linearly on the increasing concentration of CAT. The value of initial rate ($-dc/dt$) in each kinetic run was calculated from the slope of the plot of unconsumed [CAT] versus time at fixed [CAT], which is labelled as [CAT]^{*}. The value of first order rate constant (k_{obs}) in each kinetic run was calculated as:

$$k_{\text{obs}} = \frac{(-dc/dt)}{(\text{CAT})}$$

The value of rate constant approximately same to each other at different concentration of CAT (Table-1) showing first order dependence with respect to CAT. The first order rate constant (k_{obs}) increases linearly with increase in both (*p*-HBA) and Ru(III) under the experimental condition (Table-1).

TABLE-1
EFFECT OF VARIATION OF [CAT], [*p*-HBA] AND [Ru(III)] ON THE RATE OF REACTION AT 35 °C

[CAT] $\times 10^4$ (mol dm ⁻³)	[<i>p</i> -HBA] $\times 10^3$ (mol dm ⁻³)	[Ru(III)] $\times 10^6$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
1.50	3.00	1.00	2.75
2.00	3.00	1.00	2.78
2.50	3.00	1.00	2.99
3.00	3.00	1.00	2.78
3.50	3.00	1.00	2.76
1.00	1.50	1.00	1.68
1.00	2.00	1.00	2.19
1.00	2.50	1.00	2.84
1.00	3.00	1.00	3.27
1.00	3.50	1.00	3.93
1.00	3.00	1.50	2.38
1.00	3.00	2.00	3.15
1.00	3.00	2.50	4.08
1.00	3.00	3.00	4.68
1.00	3.00	3.50	5.56

Under the condition of [HClO₄] = 5×10^{-3} mol dm⁻³; [KCl] = 1×10^{-3} mol dm⁻³

Table-2 comprises the data showing the effect of variation of [H⁺] and addition of potassium chloride and *p*-toluene sulphonamide (PTS). The rate constant decreases with an increase in [HClO₄] showing inverse first order effect of [H⁺]

TABLE-2
EFFECT OF VARIATION OF [H⁺], [Cl⁻] AND ADDITION OF [PTS] ON THE RATE OF REACTION AT 35 °C

[H ⁺] $\times 10^2$ (mol dm ⁻³)	[KCl] $\times 10^3$ (mol dm ⁻³)	[PTS] $\times 10^3$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
5.00	1.00	—	2.98
6.00	1.00	—	2.65
7.00	1.00	—	2.39
8.00	1.00	—	2.12
9.00	1.00	—	1.78
5.00	0.00	—	2.16
5.00	1.00	—	2.19
5.00	1.50	—	2.15
5.00	2.00	—	2.16
5.00	2.50	—	2.10
5.00	3.00	—	2.13
5.00	3.50	—	2.18
5.00	1.00	0.00	3.33 ^a
5.00	1.00	1.00	3.53 ^a
5.00	1.00	2.00	3.46 ^a
5.00	1.00	3.00	3.15 ^a
5.00	1.00	4.00	3.87 ^a
5.00	1.00	5.00	3.27 ^a
5.00	1.00	6.00	3.36 ^a
4.00 ^a	1.00	—	2.80
4.00 ^b	1.00	—	6.47
4.00 ^c	1.00	—	11.20

Under the condition of [CAT] = 1.00×10^{-4} mol dm⁻³; [*p*-HBA] = 3×10^{-3} mol dm⁻³; [Ru(III)] = 1×10^{-6} mol dm⁻³; [*p*-HBA] = 2.50×10^{-3} mol dm⁻³; [PTS Variation]; Temp, 30° (a), 40° (b), 45° (c)

variation in its concentration range 5×10^{-2} to 9×10^{-2} mol dm⁻³. A negative [Cl⁻] effect was observed. Addition of PTS did not influence the rate. this is also evident from nearly constant k_{obs} values at different PTS. Variation of ionic strength (I) from 2×10^{-2} to 5.50×10^{-2} mol dm⁻³ shows negligible effect on rate of reaction. The reaction was studied in 30-40 °C temperature range and free energy of activation (ΔG^{\ddagger}) calculated from the rate measurements at these temperatures are given in Table-3.

TABLE-3
ACTIVATION PARAMETERS OF [Ru(III)] CATALYZED
OXIDATION OF [*p*-HBA] BY [RN NaCl] IN ACIDIC MEDIUM
UNDER THE CONDITION OF TABLES 1 AND 2 AT 35 °C

Parameters	Values
Ea (kJ mol ⁻¹)	73.68
ΔS^{\ddagger} (JK ⁻¹ mol ⁻¹)	-17.42
ΔH^{\ddagger} (kJ mol ⁻¹)	71.12
ΔG^{\ddagger} (kJ mol ⁻¹)	76.49
$A \times 10^{-13}$ (mol ⁻¹ dm ³ s ⁻¹)	9.18

Chloramine-T behaves like a strong electrolyte²⁵ and ionizes in aqueous solutions as follows:



where R = CH₃C₆H₄SO₂

Chloramine-T in acidic medium exists as following equilibria-



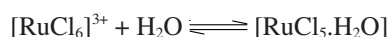
Thus in the acidified solution of chloramine-T, the possible oxidizing species are RNHCl, RNCl₂, HOCl and CAT as such. If RNCl₂ were to be reactive species, the rate law would require second order dependence on CAT, which is contrary to the experimental observations. If HOCl was to be reactive species, a first order retardation of the rate by added *para*-toluene sulphonamide would be expected which is again contrary to the observed zero effect.

Further if RNHCl was to be reactive species, then fractional order with respect to (PTS) would be required which is also contrary to observed zero effect of (PTS). Hence CAT itself may be taken as real reactive species of chloramine-T.

Ruthenium(III) chloride is reported^{26,27} to exist as [RuCl₆]³⁻ in acidic medium. Ruthenium(III) chloride exist as [Ru(H₂O)₆]³⁺ in dil. HCl²⁸. Such type of aqueous complexes are known to exist in the form of [Ru(H₂O)₅OH]²⁺ in equilibrium²⁹ with hexa aquo form.

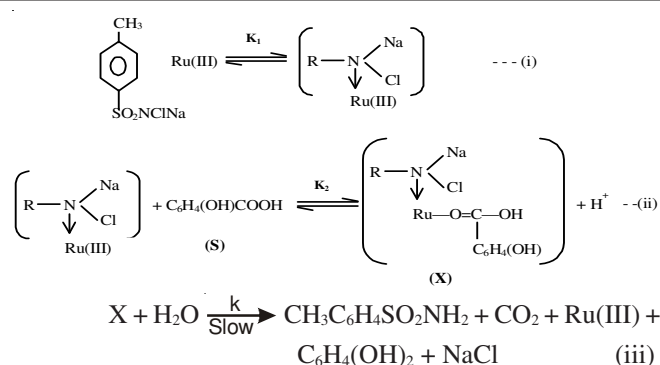


[RuCl₆]³⁻ which is in equilibrium with [Ru(H₂O)₅OH]²⁺ in the following manner³⁰.



This equilibrium in right direction would be highly favoured in acidic medium, hence [RuCl₅H₂O]²⁻ has been taken as real effective catalytic species in acidic medium.

Considering the reactive species of chloramine-T and RuCl₃ in aqueous acidic medium as well as the observed kinetic results, the following reaction scheme is suggested.



The reaction scheme of above chemical reaction in which oxidant chloramine-T first interact with catalyst Ru(III) and form complex (C₁). Then complex (C₁) react with *p*-hydroxy benzoic acid to form intermediate (X) with the removal of H⁺. Finally intermediate (X) with H₂O give product and catalyst Ru(III) regenerate. Step (iii) is slow and rate determining step. In the light of aforesaid reaction scheme, the rate of reaction may be written in terms of rate of loss of [Chloramine-T] as eqn 1.

$$-\frac{d[\text{CAT}]}{dt} = k[\text{X}] \quad (1)$$

From step (1), we have

$$K_1 = \frac{[\text{C}_1]}{[\text{CAT}][\text{Ru(III)}]} \quad (2)$$

From step (2), we have

$$K_2 = \frac{[\text{X}][\text{H}^+]}{[\text{C}_1][\text{S}]}$$

$$[\text{X}] = \frac{K_2[\text{C}_1][\text{S}]}{[\text{H}^+]} \quad (3)$$

where S = *p*-hydroxy benzoic acid. By comparing eqns 2 and 3, we have

$$[\text{X}] = \frac{K_1 K_2 [\text{CAT}][\text{Ru(III)}][\text{S}]}{[\text{H}^+]} \quad (4)$$

On substituting the value of [X] from eqn 4 in eqn 1, we have eqn 5.

$$-\frac{d[\text{CAT}]}{dt} = \frac{k K_1 K_2 [\text{CAT}][\text{Ru(III)}][\text{S}]}{[\text{H}^+]} \quad (5)$$

The rate expression eqn 5 fully explains all observed kinetic data. It explains first order kinetics with respect to oxidant, first order with respect to substrate, first order with respect to catalyst and inverse first order kinetics with respect to [H⁺] *i.e.* medium. Thus, the mechanism seems to be valid.

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