Study of Effect of Variation of Ionic Strength of the Medium on Velocity Constant of Ru(III) Catalyzed Oxidation of Hydroxy Benzoic Acids by Chloramine-T in Acidic Medium

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ABSTRACT

In the present study the effect of variation of ionic strength of the medium on rate of oxidation of hydroxy benzoic acids as its effect provides some clues regarding the nature of reactive species involved in the rate determining step. In order to realize the above aim the experiments has been carried out which ultimately concluded that ionic strength variation does not change the reaction velocity constant significantly.

Key words: Ortho-hydroxy bezoic acid (0-HBA), meta-hydroxy bezoic acid (m-HBA), para-hydroxy bezoic acid (p-HBA),Ruthenium chloride (Ru(III)), Chloramine-T (CAT), perchloric acid ($HClO_4$), Pottassium chloride (Kcl),sodium perchlorate ($NaClO_4$).

INTRODUCTION

Ionic strength

The rate of reaction between charged species are affected strongly by the ionic strength of the solution, which is defined as: – $I = \frac{1}{2} \Sigma\, c_i\, Z_i^2$

where c_i is the concentration of each ion present in the solution and Z_i is its charge number. When the reacting species are of the same sign, an increase in ionic strength increases the rate, when ions of opposite signs react, there is a decrease in rate with increasing ionic strength. Bronsted, Bjerrum, Christiansen, Davis and Scatchard suggested that the rate of reaction between species A and B should be expressed as –

$$v = k_0[A][B]\gamma_A, \gamma_B, \gamma_x \ and\ \gamma_i \quad ...(1)$$

where k_0 is a constant at a given temperature, g_A and g_B are the activity coefficient of the reactant and g_x is collision complex. According to Debye-Huckel theory, the activity coefficient g_i of an ion is related to the ionic strength by the equation –

$$\log \gamma_i = - B\, Z_i^2\, I^{1/2} \quad\quad ... (2)$$

where z_i is the charge number of the ion and B is a quantity, whose value can be calculated from Debye-Huckel equation. From equation (1) the rate constant k (=v//[A] [B]) is -

$$k = k_0 \frac{\gamma A \, \gamma B}{\gamma x} \qquad \text{... (3)}$$

$$Log \frac{k}{k_0} = 1.02 \, Z_A \, Z_B \, (I/\text{mol.dm}^{-3})^{1/2} \qquad ...(5)$$

which is logarithmic form including equation (2) becomes-

$$\log k = \log k_0 + 2 \, B \, Z_A \, Z_B \, I^{1/2} \qquad ...(4)$$

For an aqueous solution at 25°C this equation becomes –

According to equation (5) a plot of log k versus (I/mol. dm^{-3})$^{1/2}$ will give a straight line of slope 1.02 $Z_A Z_B$ and intercept is log k_0. If one of the reactants is a neutral molecule, $Z_A Z_B$ is zero and the rate constant is expected to be independent of the ionic strength. The rate constant of a reaction between an ion and a neutral molecule should vary

Table 1 (a):

[o-HBA] = 5.00×10^{-3} mol dm^{-3} [HClO$_4$] = 2.00×10^{-3} mol dm^{-3}
[CAT] = 1.00×10^{-4} mol dm^{-3} [Ru(III)] = 1.00×10^{-6} mol dm^{-3}
[KCl] = 1.00×10^{-3} mol dm^{-3}

[NaClO$_4$] × 10^3 mol dm^{-3}	Ionic strength (μ × 10^3) mol dm^{-3}	(−dc/dt) × 10^8 mol dm^{-3} s^{-1}	k$_1$ × 10^4 s^{-1}
0.00	2.00	1.56	2.00
1.00	3.00	1.77	2.27
1.50	3.50	1.73	2.22
2.00	4.00	1.53	1.96
2.50	4.50	1.51	1.94
3.00	5.00	1.59	2.06
3.50	5.50	1.66	2.13

[CAT]* = 7.80 × 10^{-5} mol dm^{-3} at which (−dc/dt) has been calculated.

Table 1 (b):

[m-HBA] = 1.00×10^{-3} mol dm^{-3} [HClO$_4$] = 6.00×10^{-3} mol dm^{-3}
[CAT] = 1.00×10^{-4} mol dm^{-3} [Ru(III)] = 1.00×10^{-6} mol dm^{-3}
[KCl] = 1.00×10^{-3} mol dm^{-3}

[NaClO$_4$] × 10^3 mol dm^{-3}	Ionic strength (μ × 10^3) mol dm^{-3}	(−dc/dt) × 10^8 mol dm^{-3} s^{-1}	k$_1$ × 10^4 s^{-1}
0.00	6.00	0.89	1.00
0.50	6.50	0.92	1.03
1.50	7.50	0.90	1.01
2.50	8.50	0.93	1.04
3.50	9.50	0.96	1.07
4.50	10.50	0.94	1.05
5.50	11.50	0.97	1.08

[CAT]* = 8.90 × 10^{-5} mol dm^{-3} at which (−dc/dt) has been calculated.

with the first power of the ionic strength instead of with the square root. $k = k_0 (1+bI)$ so the rate constant should vary linearly with I.

Chloramine-T is the sodium derivative of N-chloro p-toluene sulphonamide $CH_3C_6H_4SO_2NCl$ $Na.3H_2O$ (molecular weight 281.70), prepared easily and mainly from p-toluene sulphonic acid, a cheap by product in the manufacture of saccharin. It is a less familiar but very potent oxidizing agent in alkaline as well as in acid media. A survey of existing literature showed that chloramine-T has been used for the determination of numerous inorganic and organic substances. It has been reported that in acidic medium (Hydrochloric acid), $[RuCl_6]^{-3}$ is taken as

reactive species. For the sake of simplicity, $[RuCl_6]^{-3}$ is written as [Ru(III)] in the same scheme. Ru(III) chloride exists as $[Ru(H_2O)_6]^{3+}$ in dil. HCl. Such type of aqueous complexes are known to exist in the form $[Ru(H_2O)_5OH]^{2+}$ in equilibrium with hexa aquo form.

$$[Ru(H_2O)_6]^{3+} \rightleftharpoons [Ru(H_2O)_5OH]^{2+} + H^+$$
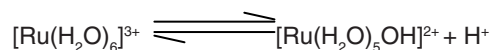
$[RuCl_6]^{-3}$ which is in equilibrium with $[Ru(H_2O)_5OH]^{-2}$ in the following manner.

$$[RuCl_6]^{-3} + H2O \rightleftharpoons [RuCl_5.H_2O]^{2-} + Cl^-$$
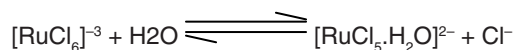
Table 1(c):

[p-HBA] = 2.00×10^{-3} mol dm^{-3} [HClO$_4$] = 2.00×10^{-3} mol dm^{-3}
[CAT] = 1.00×10^{-4} mol dm^{-3} [Ru(III)] = 1.00×10^{-6} mol dm^{-3}
[KCl] = 1.00×10^{-3} mol dm^{-3}

Temperature – 35°C			
[NaClO$_4$] × 10^3 mol dm^{-3}	Ionic strength (μ × 10^3) mol dm^{-3}	(–dc/dt) × 10^8 mol dm^{-3} s^{-1}	k$_1$ × 10^4 s^{-1}
0.00	4.00	2.63	3.46
1.00	5.00	2.60	3.42
2.00	6.00	2.53	3.32
3.00	7.00	2.56	3.36
4.00	8.00	2.65	3.48
5.00	9.00	2.75	3.61
6.00	10.00	2.55	3.35

[CAT]* = 7.60×10^{-5} mol dm^{-3} at which (–dc/dt) has been calculated.

This equilibrium in right direction would be highly favoured in acidic medium, suggesting that $[RuCl_5.H_2O]^{2-}$ in the actual reactive species of Ruthenium (III) chloride in present work.

EXPERIMENTAL

To determine the effect of variation of Ionic strength of velocity content of Ru(III) Catalysed oxidation of hydroxyl benzoic acid the various experiments with varying ionic strength (affected by addition of suitable amount of sodium perchlorate) at constant concentration of other reactants have been carried out in oxidation of each hydroxyl benzoic

acid and the result have been reported in table A,B and C respectively in ortho- hydroxy benzoic acid, meta- hydroxy benzoic acid, para-hydroxy benzoic acid in a summarized way.

CONCLUSION

It is clear from the result of the tables A, B & C that upon increasing the concentration of sodium perchlorate, the ionic strength variation does not change the reaction velocity constants significantly. Thus there is neglicence effect of ionic strength of the medium on reaction.

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