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Study of Rapid Iodination of Uracil and Cytosine Nucleobases by Molecular Iodine in Aqueous Medium by Hydrodynamic Voltammetry

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Abstract—*The detailed kinetic study of pyrimidine nucleobases cytosine and uracil with molecular iodine bya rotating platinum electrode has been obtained. The iodinated nucleobases have various pharmaceutical applications. Hence it is important to study them. In this paper we have used a voltammetry method to observe the reaction kinetics of these reactions. The kinetic and thermodynamic parameters have been obtained.*

Keywords: *Hydrodynamic Voltammetry, Saturated Calomel Electrode (SCE), Rotating Platinum Electrode (RPE), Uracil, Cytosine.*

INTRODUCTION

Nucleic acids are important in the nature as they serve the function of regulation of human body reactions. Nucleobases are heterocyclic molecules attached to nucleotides of nucleic acids. Halogenated nucleobases serve the pharmaceutical industry from decades because of various medicinal and veterinary applications [1,2].

Iodinated nucleobases have also various applications, 5-iodinated pyrimidine derivatives are used as drugs [3] and radio labelled iodinated derivatives are used as scanning agents in medical diagnosis. The halogenated species generate 5- substituted derivatives of pyrimidine nucleobases. Hence it remains important to study these reactions.

In this paper we have observed the reaction kinetics of two pyrimidine nucleobases uracil and cytosine with molecular iodine in aqueous medium. These reactions seem to be rapid and hydrodynamic voltammetry is used to observe the rapid kinetics of these two reactions [4]. The method uses rotating platinum electrode rotated at high speed by A.C motor and saturated calomel electrode as reference electrode[4,5].

INSTRUMENTS USED

The following instruments were used in the whole experiment.

1. Hydrodynamic voltammetry instrumentation.
2. pH meter from Elico India.

CHEMICALS USED

Uracil and Cytosine nucleobases were purchased from Himedia India, supportingelectrolyte KNO_3 from Fischer Scientifics, citric acid and sodium dihydrogen phosphate from Merck. The entire chemicals purchased were of A.R grade.

PREPARATION OF SOLUTIONS

2×10^{-3} M solution of both uracil and cytosine were prepared in double distilled water and were labelled as stock solution. Phosphate buffer components, citric acid and sodium dihydrogen phosphate were prepared in double distilled water.

Molecular iodine was prepared by dissolving iodine crystals in double distilled water and keptovernight [6]. The concentration of I_2 was obtained by iodometry.

KINETIC MEASUREMENTS FOR CYTOSINE

3.1×10^{-5}M 50 ml of both cytosine and I_2 were prepared from stock solutions in separate containing the supporting electrolyte and phosphate buffer to maintain 7 pH. Cytosine solution were taken and transferred to the reaction cell containing RPE and SCE electrodes. A small potential of 0.1V were applied [4-7]. The I_2 solution were taken out and added to the cytosine solution and immediately stop watch was started. The readings from the scale were obtained every 10 seconds.

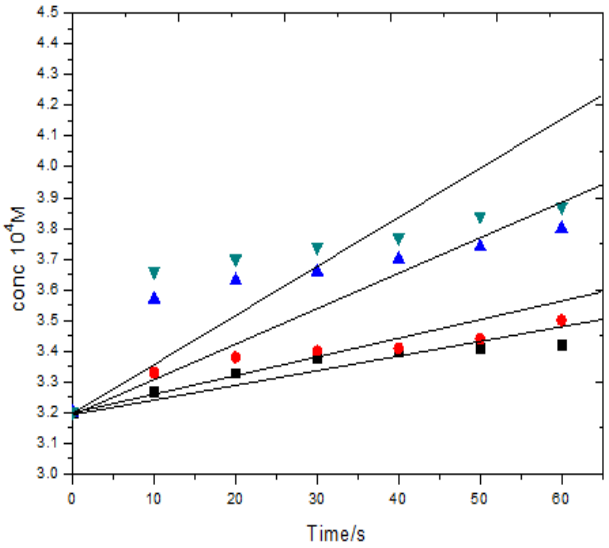

Figure 1: Kinetics of Cytosine iodination at various temperatures.

Calculation for the slope of graph

The figure above is the kinetic graphs of the cytosine at varying temperatures. The slope of the each line indicated in the figure is the specific reaction rate at that temperature and slope of the graph was calculated by $\frac{\Delta y}{\Delta x}$ at all temperatures. The calculated specific reaction rates are given in table.

Table 1: Calculated specific reaction rates at different temperatures.

Temperature /^{0}C	Temperature/ K	$[T]^{-1}/10^{-3}$	k (specific reaction rate)	Log k
25	298	3.35	26	1.41
31	304	3.28	40	1.60
37	310	3.22	78	1.89
41	314	3.18	89	1.94

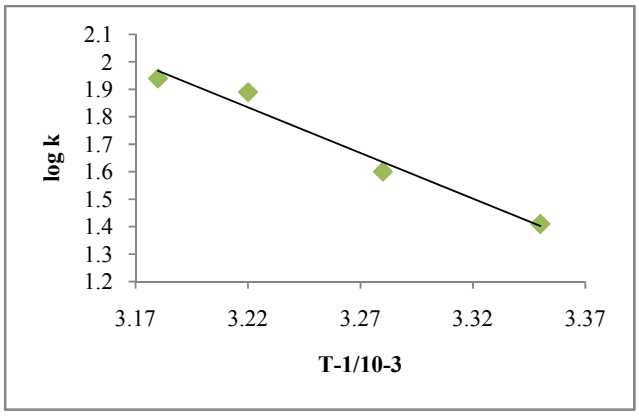

Figure 2: Variation of log k versus T^{-1}

Calculation for Activation energy (Ea) at 25^{0}C:

Slope calculated from Arrhenius plot

Slope = (-3400)

Activation energy (Ea) = -2.303 (slope) ×R×T

Where R is gas constant and T temperature in Kelvin

Ea = -2.303× (-3400) ×8.314×298

Ea = 65100.28 J

Ea = 65.10 kJ.

Calculation for frequency factor (A) at 25^{0}C:

Frequency factor from equation $k = A\, e^{-(Ea/RT)}$

Where k is specific rate constant.

Ea is activation energy in joules.

R represents gas constant.

T is temperature in Kelvin.

Inserting the value in equation the equation becomes $k = A\, e^{-(65100.28/8.314\times298)}$

$k = A\, e^{-(26.26)}$

$k = A\ 3.93\times10^{-12}$

$A = 26 / 3.93\times10^{-12}$

$A = 6.61\times10^{12}$

Table 2: Kinetic parameter of Cytosine at 25^{0}C

Kinetic parameter	Value
Specific reaction rate/ $M^{-1}\ s^{-1}$	26
Activation energy/ kJ/mol^{-1}	65.10
Frequency factor/ $M^{-1}s^{-1}$	6.61×10^{12}

KINETICS OF IODINATION OF URACIL

1×10^{-4} M 50 ml both of uracil and I_2 was placed in separate bottles in thermostat to attain the required temperature. I_2solution was transferred to reaction vessel containingRPE and SCE electrodes and a potential of 0.1V was applied by D.C battery .The reading on the scale was adjusted by a shunt [7]. The uracil solution was then transferred to the reaction vessel and immediately a stop watch was started. The reading on scale was taken every 10 seconds. The whole experiment was repeated at varying temperatures.

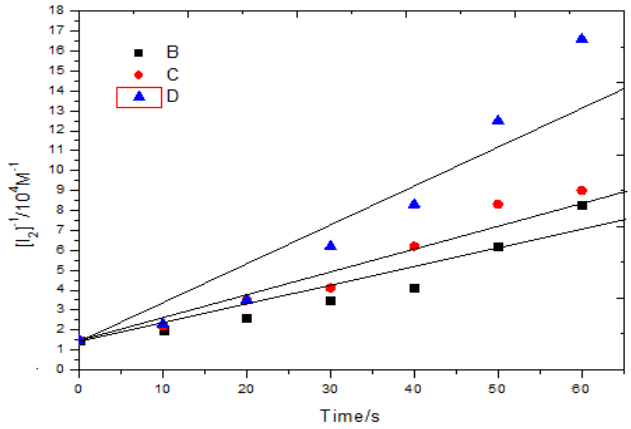

Figure 3: Kinetics of Uracil iodination at various temperatures

Table 3: Specific reaction rates at different temperatures

Temperature /^{0}C	Temperature/ K	$[T]^{-1}/10^{-3}$	k (specific reaction rate)	Log k
27	300	3.33	1050	3.01
30	303	3.30	1325	3.12
34	307	3.25	2450	3.38

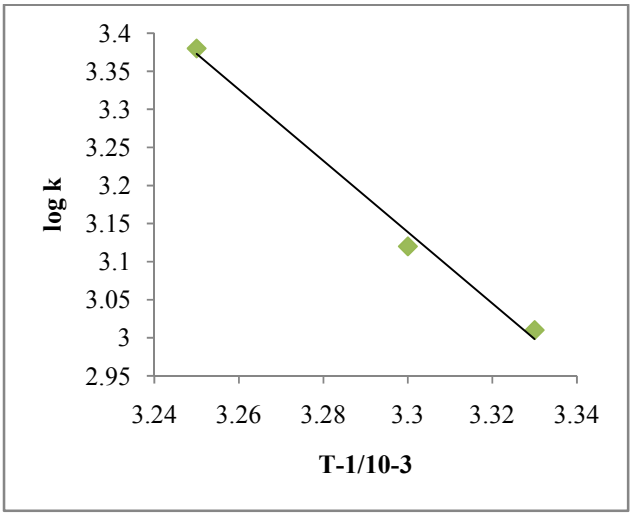

Figure 4: Variation of log k versus T^{-1} in Kelvin.

Table 4: Kinetic parameter of Cytosine at 27^{0}C

Kinetic parameter	Value
Specific reaction rate /M^{-1} s^{-1}	1050
Activation energy/ kJ/mol^{-1}	47.75
Frequency factor/ $M^{-1}s^{-1}$	2.15×10^{11}

CONCLUSIONS

This paper is the detailed kinetic study of iodination of two nucleobases (Uracil and Cytosine) in aqueous medium, It has been observed that both the reactions follow second order kinetics and are fast, it was not possible to determine these fast reactions by classical methods, so a simple method is used here to study the reaction kinetics of these two biological important molecules in a very short span of time.

The specific reaction rates and other thermodynamic parameters have also been calculated.

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