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Kinetic study of the rapid bromination of adenine nucleobase by molecular bromine in aqueous medium

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Abstract
The kinetic study of the bromination of two nucleobases uracil and adenine both pyrimidine nucleobase by molecular bromine in aqueous medium using a rotating platinum electrode (RPE) has been carried out. The kinetic and related thermodynamic parameters of these reactions have been evaluated.

Keywords: Bromination, nucleobase, RPE

1. Introduction
Halogenated nucleobases serve an important application in pharmaceutical industry as they are used as antiviral, anticancer and antifungal drugs [1]. These nucleobases are heterocyclic molecules which are present in nucleic acids of all living beings ranging from unicellular bacteria to highest living chordates [2]. There are five types of nucleobases including DNA and RNA. These are cytosine, uracil and thymine which are single ring pyrimidine compounds and adenine, guanine which are bicyclical purine compounds [2-3]. The main function of nucleobases in living systems is to express genetic coding which is the basis for the protein synthesis and expression of character with hereditary [2-4].
Halogenations of nucleobases have been carried by various regents in different reaction mediums and it has been observed that halogenations in case of pyrimidine rings occurs at 5 position and for purine rings it occurs at 8-position. These reactions mainly follow aromatic electrophillic substitution mechanism and the halogen atom is substituted for the proton in these positions [6]. Herein we have observed the bromination of uracil and adenine nucleobases by molecular bromine in aqueous medium at neutral pH. The focus of our study is to determine the reaction kinetics of both the reactions and confirm the nature of the halogenated products by FT-IR and NMR studies. As these reactions are rapid in aqueous medium, it is impossible to observe the kinetics by conventional methods. Hence the voltammetry technique has been used to investigate the rapid kinetics using a rotating platinum electrode [7-8]. In this method a platinum electrode is rotated at a high speed of 650 RPM by an A.C motor and the fall in concentration of the molecular halogen species is observed in terms of the diffusion using a galvanometer lamp and scale arrangement [8-9]. The readings detect the fall in concentration of the electro-active species in the reaction medium, in this case the bromine molecule.

2. Materials and methods.
Instruments
Hydrodynamic voltammetry instrumentation including rotating platinum electrode and pH meter from Elico India were used.

Chemicals
Uracil and Adenine nucleobases were purchased from Himedia India, supporting electrolyte KNO_3 from Fischer Scientifics, citric acid and sodium dihydrogen phosphate from Merck. The chemicals purchased were of A.R grade.

Preparation of solutions

2×10^{-3} M solution of uracil and adenine were prepared in double distilled water. The phosphate buffer components citric acid 0.2M and sodium dihydrogen phosphate 0.1M solutions were also prepared [5].

Aqueous Br_2 solution was prepared by dissolving liquid bromine in double distilled water and the concentration obtained was determined by iodometry [10].

Calibration of diffusion current: Aqueous Br_2 solutions of varying concentrations were prepared and the diffusion current due to these at the RPE was noted in terms of the deflection of a galvanometer light spot on the scale [6-9]. The SCE was the reference electrode. The calibration results obtained are given in the ensuing Tables and Figures.

Table 1: Calibration of Br_2 Solutions

Conc. of $[Br_2]$ / 10^{-6} M	Mean Galvanometer deflection / cm
1.0	2.0
1.5	3.0
2.5	5.0
.0	10
7.5	15
10	20
20	40

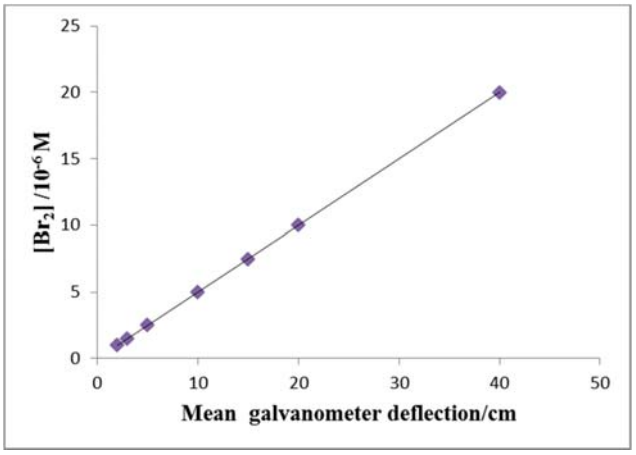


Fig 1: Calibration Plot

Kinetic study of Adenine nucleobase

3×10^{-5}M 50 ml of both adenine and Br_2 were kept in the thermostat in different stoppered flasks to attain the required temperature.First the defection on the scale due to 1.5×10^{-5}M 100 ml of Br_2 was adjusted to 40 cm on galvanometer using a shunt. Then the two reactants were mixed in a reaction cell containing the RPE and SCE and the reading on the scale was noted at every 10 seconds [12]. The kinetic data was obtained for different temperatures. Typical data are presented in Tables 2 and 3.

Table 2: Kinetics of Adenine bromination at 20 ^{0}C.

Time/s	Mean Galvanometer deflection/ cm	$[Br_2]$ /10^{-6}M	$[Br_2]/10^4$ M^{-1}
0	20.0	15..0	6.60
10	15.5	11.6	8.60
20	14.2	10.6	9.40
30	13.4	10.0	10.0
40	13.0	09.7	10.2
50	12.3	09.2	10.8
60	11.6	08.7	11.4

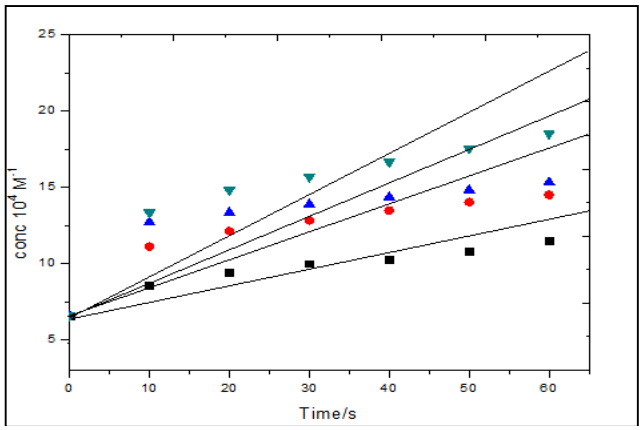


Fig 2: *Kinetics of Adenine bromination at various temperatures*

Calculation for specific reaction rate

The slope of the plot of $[Br_2]^{-1}$ versus time 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 3.

Table 3: Specific reaction rates at different temperatures.

Temperature/ ^{0}C	Temperature/K	$[T]^{-1}/10^{-3}$	k (specific reaction rate)	Log k
20	293	3.41	600	2.77
24	297	3.36	1100	3.04
28	301	3.32	1150	3.06
30	303	3.30	1600	3.20

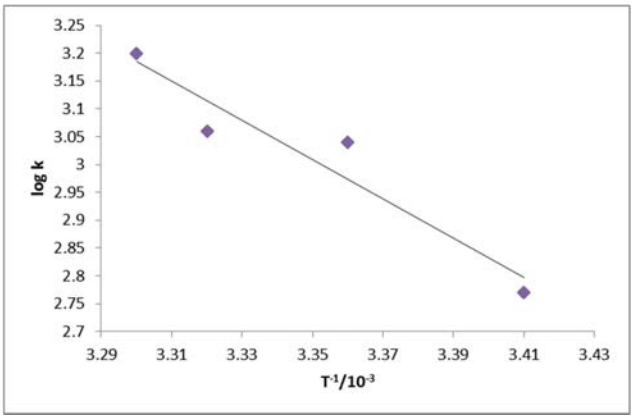


Fig 3: Variation of log k versus T^{-1}

Calculation for Activation energy (Ea) at 24 ^{0}C

Slope calculated from Arrhenius plot

Slope = (-3500)

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

Where R is gas constant and T temperature in Kelvin

Ea = -2.303× (-3500) ×8.314×297

Ea = 67014 J

Ea = 67.014 kJ.

Calculation for frequency factor (A) at 24 ^{0}C

Frequency factor can be calculate by 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.

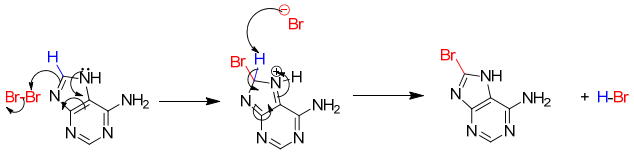
$k = A\, e^{-(27.13)}$

$A = 6.66\times10^{14}$.

Table 7: Kinetic parameters of Adenine at 24 ^{0}C

Kinetic parameter	Value
Specific reaction rate /M^{-1} s^{-1}	1100
Activation energy/ kJ/mol^{-1}	67.01
Frequency factor/ $M^{-1}s^{-1}$	6.66×10^{14}

Suggested reaction mechanism for bromination of adenine.



3. Conclusion

The bromination kinetics of two nucleobases uracil and adenine in aqueous medium by hydrodynamic voltammetry has been studied. The specific reaction constant at different temperatures has beenevaluatedd for both the rapid reactions. The suggested mechanism indicating the mono-bromo derivatives formation has been confirmed by FT-IR and NMR spectroscopy. Related thermodynamic parameters, activation energy and frequency factor have been also calculated.

4. References

1. Joytirmoy M, Roger S, Molecule. 2013; 18:12740
2. Cooper MG, Hausman ER. The Cell a Molecular Approach, Sinauer Assoicates & Sunder Massachusetts, 2009.
3. Lodish H, Berk A, Kaiser AC, Montu K, Scott PM, Bretscher A *et al*. Molecular Cell Biology, W.H Freeman & Company New York, 2008.
4. Michael MC, David LN. Lehninger Principles of Biochemistry, W H Freeman & Company New York, 2008
5. Verma AS, Das S, Sing A. Laboratory Manual for Biotechnology. 2014.
6. Borkar VT, Dangat VT, Bonde SL, Bhadane RP. Res. J. Chem. Sci. 2014; 4:77
7. Saxena DR, Bahule BB, Borkar VT, Dangat VT. J. Curr. Chrm. Pharma. Sc. 2015; 5:105.
8. Yadav RP, Bhorkar VT, Dangat VT, Mondal T. International Journal of Science and Research. 2015; 4:217
9. Bonde SL, Bhadane RP, Dangat VT, Sukul TM. International Journal of Science Education and Research. 2014; 3:797.
10. Maske PD, Sangpal RR, Borkar VT, Dangat VT, Int. Res. J. Science and Engineering. 2015; 3:197.
11. Borkar VT. IJCPS. 2015; 3:1957.
12. Ghorpade VS, Borkar VT, Dangat VT. Int. J. Curr. Res. Chem. Pharma. Sci. 2015; 2:22.