Kinetic study of Oxidation of some Monosaccharides by Chloramine-T induced by Visible light source

Wadhwani Meena[1] and Jain Shubha[2],
[1]Advance College of Science & Commerce, Ujjain, MP, INDIA
[2]School of Studies in Chemistry & Biochemistry, Ujjain, MP, INDIA

Abstract

The kinetics of photochemical oxidation of glucose and fructose by chloramine-T in acidic medium has been studied. The reaction mixture including known quantity of substrate (glucose/fructose), acid and chloramine-T was taken in the vessel and irradiated in the visible light source. The course of the reaction was followed at definite interval by titrating the reaction mixture against standard hypo solution using starch as an indicator. The reaction has a first order dependence on chloramine-T. With excess concentration of other reactants, the reaction rate follows first order kinetics with respect to substrate. The reaction is catalysed by H^+ ions as well. A small salt effect and increase in reaction rate with increasing the intensity of light source is also observed. Addition of p-toluene sulphonamide retards the reaction rate. On the basis of product analysis, a pertinent mechanism is proposed.

Keywords: Kinetics, photochemical oxidation, glucose, fructose, chloramine-T.

Introduction

Carbohydrates are the essential biomolecules and a chief source of energy for living system[1]. The oxidation of carbohydrates and fats in living system is a free radical reaction and we get energy from these exothermic reactions[2]. Thus the oxidation of carbohydrates is a basic source of life.

Chloramine-T (p-Me-$C_6H_4SO_2N$-ClNa) generally written as CAT is a versatile oxidizing agent. The sodium derivative of N-chloro-p-toluene sulphonamide is generally known as the Chloramine-T and represented as follows
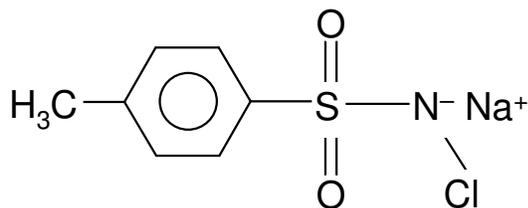
During last few years' interest has been focused upon the studies in the mechanism of carbohydrates which led to the preparation of its degradation products or its complete breakdown. The oxidation of carbohydrates has been studied by various workers using a variety of oxidizing agents[3-29] but the photochemical oxidation with chloramine-T as an oxidant has not been investigated. Therefore we have chosen CAT to study the oxidation of some carbohydrates in presence of light. The present work deals with the kinetics of photochemical oxidation of two monosaccharides i.e. glucose and fructose.

Material and Methods

The chemicals used were of analar grade and the reagent solutions were prepared in doubly distilled water. The required volumes of glucose/fructose, CAT, HCl and other reagents, where necessary, were mixed in a 250 ml beaker. The reaction vessel was kept under visible light source (tungsten lamp). The course of the reaction was followed by withdrawing 2 ml of reaction mixture at a definite time interval and adding it to a flask containing potassium iodide solution to quench the reaction. The unreacted chloramine-T quickly reacts with KI solution and liberates iodine which was titrated against standard sodium thio sulphate solution as titrant using starch as indicator.
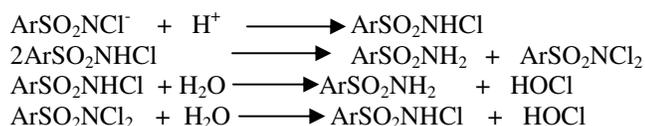
Analysis of reaction products: Glucose/fructose (9g/100ml), CAT (0.563 gm/100ml) and water were mixed in a flask and the flask was kept under tungsten lamp. After completion of the reaction (as indicated by TLC), the light source was removed. The spots obtained on the TLC plate were found to be of formaldehyde and formic acid by co-TLC with the authentic samples. The products were further confirmed by qualitative tests. The development of reddish brown color with Nessler's reagent changing to yellow green confirms formaldehyde as one of the reaction product. The development of red color with ferric chloride solution and also the evolution of carbon monoxide with conc. H_2SO_4, which was confirmed by flame test, indicate the formation of formic acid as another product.

Results and Discussion

Chloramine-T is a strong electrolyte. It dissociates in aqueous solution as follows

$$ArSO_2NClNa \longrightarrow ArSO_2NCl^- \quad + \quad Na^+$$

The anion picks up a proton in acidic medium to give free acid

$$ArSO_2NCl^- + H^+ \longrightarrow ArSO_2NHCl$$
$$2ArSO_2NHCl \longrightarrow ArSO_2NH_2 + ArSO_2NCl_2$$
$$ArSO_2NHCl + H_2O \longrightarrow ArSO_2NH_2 + HOCl$$
$$ArSO_2NCl_2 + H_2O \longrightarrow ArSO_2NHCl + HOCl$$

The CAT generates HOCl, which is the oxidizing species of the reaction. The reaction was carried out by varying the concentration of all the reactants and the following results have been obtained:

Reaction order with respect to chloramine-T: In a typical kinetic run, a straight line was obtained by plotting log (a-x) versus time, indicating that the reaction under the chosen conditions follows pseudo first order kinetics. The order with respect to oxidant is unity table 1.

Effect of variation of oxidant (chloramine-T) concentration: By keeping the concentration of other reactants constant, only the concentration of oxidant is varied from 3.7×10^{-3} to 10.0×10^{-3}. The rate constants were calculated at definite time intervals. The results obtained are summarized in table-1.

Table-1
Effect of variation of oxidant (chloramine-T) concentration

S.No.	$[CAT] \times 10^3$ M	$k \times 10^4$ sec^{-1} (For Glucose)	$k \times 10^4$ sec^{-1} (For Fructose)
1	3.7	2.06	2.34
2	5.0	2.36	2.77
3	6.2	2.78	3.27
4	7.5	3.31	3.80
5	8.8	3.89	4.30
6	10.0	4.60	4.58

[Glucose/Fructose] = 5.0×10^{-3} M   [HCl] = 1.0×10^{-3} M

The results reveal that the value of rate constant increases as the concentration of CAT increases. It is because the increase in [CAT] generates more HOCl which acts as an oxidizing species.

Reaction order with respect to substrate: On varying the concentration of glucose/fructose from 1.2×10^{-3} to 7.5×10^{-3}, an increase in reaction rate was observed. The plot of log k versus [substrate] gave a straight line with a slope suggesting that the order with respect to substrate is one table 2.

Effect of variation of substrate concentration: The concentrations of other reactants were kept constant and only the concentration of substrate (glucose/fructose) was varied from 1.2×10^{-3} to 7.5×10^{-3}. The rate constants were calculated at definite time intervals. The results obtained are summarized in table 2.

Table-2
Effect of variation of substrate concentration

S.No.	[Glucose/ Fructose] 10^3 M	$k \times 10^4$ sec^{-1} (For Glucose)	$k \times 10^4$ sec^{-1} (For Fructose)
1	1.2	3.39	3.31
2	2.5	3.72	3.63
3	3.7	4.02	4.25
4	5.0	4.60	4.58
5	6.2	5.08	5.10
6	7.5	5.70	5.59

[CAT]=10.0×10^{-3} M   [HCl] = 1.0×10^{-3} M

Reaction order with respect to acid: On varying the hydrochloric acid concentration from 1×10^{-3} to 5.0×10^{-3}, an increase in reaction rate was observed. The plot of log k versus [H$^+$] gave a straight line suggesting that the reaction is catalyzed by acid table 3.

Effect of variation of acid concentration: The kinetics of reaction was also studied by varying the concentration of acid and keeping that of oxidant and substrate constant. The rate constants were calculated at definite time intervals. The results obtained are summarized in table 3.

Table-3
Effect of variation of acid concentration

S.No.	$[HCl] \times 10^3$ M	$k \times 10^4$ sec^{-1} (For glucose)	$k \times 10^4$ sec^{-1} (For Fructose)
1	0.2	2.40	2.55
2	0.4	2.80	2.97
3	0.6	3.35	3.39
4	0.8	3.96	3.88
5	1.0	4.60	4.58

[CAT]=10.0×10^{-3} M   [Glucose/Fructose] = 5.0×10^{-3} M

Effect of variation of Cl$^-$ ion concentration: The role of chloride ion in the kinetics of the oxidation reaction by CAT is very crucial. The straight lne obtained in the plot of log k versus [Cl$^-$] indicates an increase in reaction rate with increase in Cl$^-$ ion concentration. The cause of speeding up in reaction rate is the generation of HOCl due to the interaction between a chloride ion and a chloronium ion produced by the hydrolysis of N-Cl bond table 4.

Salt Effect - Effect of variation of concentration of KCl: The concentrations of other reactants were kept constant and only the concentration of KCl was varied from 0.4×10^{-3} to 1.0×10^{-3}. The rate constants were calculated at definite time intervals. The results obtained are summarized in table 4.

Table-4
Salt Effect - Effect of variation of concentration of KCl

S.No.	[KCl]x 10^3 M	k x 10^4 sec^{-1} (For Glucose)	k x 10^4 sec^{-1} (For Fructose)
1	0.4	3.86	3.10
2	0.6	4.25	3.43
3	0.8	4.65	3.76
4	1.0	5.00	4.42

[CAT]=10.0×10^{-3} M   [Glucose/Fructose] = 5.0×10^{-3} M [HCl]= 1.0×10^{-3} M

Effect of addition of p-toluene sulphonamide (PTS): The addition of PTS, one of the reaction products, from 1.0×10^{-3} to 4.0×10^{-3} at constant CAT and substrate concentration, decreases the reaction rate. This decrease is the result of mass-law effect according to which the addition of product causes the reversal of reaction and hence the reaction proceeds in backward direction[30]. This further confirms the hypochlorous acid (HOCl) as being the main oxidizing species during the phototchemical oxidation by chloramines-T in acidic medium table 5.

Kinetics and activation parameters: The values of enthalpy of activation, entropy of activation and free energy of activation give an idea about the progress of reaction. It has been observed that if ΔH^* is positive, ΔS^* is negative and ΔG^* is positive then the reaction is non spontaneous[31]. This fact has been confirmed by carrying out the reaction without heat and light and no reaction was observed in that condition which shows that the reaction needs some initiation which can be provided by means of light or heat table 6.

Effect of variation of product concentration: p-Toluene sulphonamide (PTS) is considered as a major product during the oxidation reactions by chloramine-T. Therefore the addition of PTS also affects the reaction rate. The reaction was studied by keeping the concentrations of other reactants constant and only the concentration of PTS was varied from 0.4×10^{-3} to 1.0×10^{-3}. The rate constants were calculated at definite time intervals. The results obtained are summarized as follows.

Table-5
Effect of variation of product concentration
[CAT]=10.0×10^{-3} M [Glucose/Fructose] = 5.0×10^{-3} M[HCl]= 1.0×10^{-3} M

S.No.	[PTS]x 10^3 M	k x 10^4 sec^{-1} (For Glucose)	k x 10^4 sec^{-1} (For Fructose)
1	0.4	3.44	3.29
2	0.6	3.17	2.98
3	0.8	2.88	2.69
4	1.0	2.56	2.42

Activation Parameters: Different kinetics and activation parameters were calculated using the experimental findings and their values are given in table below for glucose and fructose both.
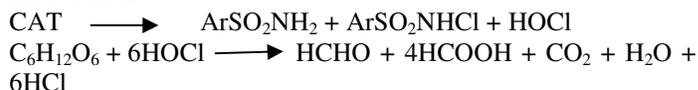
Table-6
Activation Parameters

Activation Parameter	Glucose	Fructose
Energy of activation (Ea)	20.046 KJ mol^{-1}	13.783 KJ mol^{-1}
Frequency factor (log PZ)	3.986	2.909
Enthalpy of activation (ΔH^*)	17.48 KJ mol^{-1}	11.22 KJ mol^{-1}
Entropy of activation (ΔS^*)	-172.5 JK^{-1} mol^{-1}	-193 JK^{-1} mol^{-1}
Free energy of activation (ΔG^*)	70.61KJ mol^{-1}	70.66 KJ mol^{-1}

Mechanism: On the basis of experimental findings and results a tentative mechanism has been proposed for the photochemical oxidation of some carbohydrates by chloramine-T.

The mechanism for the dissociation of CAt giving HOCl has already been given. The HOCl dissociates photochemically into free radicals as follows:

$$HOCl \longrightarrow OH^\bullet + Cl^\bullet$$

These OH$^\bullet$ radicals bring about the oxidation of carbohydrates. The Cl$^\bullet$ radicals combine with the H$^\bullet$ radicals produced during oxidation to give HCl which has been detected by bringing the rod dipped in NH_4OH on the flask. The evolution of CO_2 has been confirmed by lime water test. The overall reaction for the oxidation is:

$$CAT \longrightarrow ArSO_2NH_2 + ArSO_2NHCl + HOCl$$
$$C_6H_{12}O_6 + 6HOCl \longrightarrow HCHO + 4HCOOH + CO_2 + H_2O + 6HCl$$

Conclusion

The kinetic study of photochemical oxidation of monosaccharides by CAT in visible light confirms that the reaction order with respect to oxidant as well as the substrate is one. The reaction rate shows enhancement with the increase in concentration of acid. Further, due to photochemical condition, the reaction follows radical mechanism. The reaction velocity accelerated with increase in the intensity of light source. The values of different activation parameters viz. enthalpy of activation, entropy of activation and free energy of activation give an idea about the progress of reaction. It has been reported that when ΔH^* is positive, ΔS^* is negative and ΔG^* is positive then the reaction is non spontaneous. The above fact has been confirmed by placing the reaction system in dark at room temperature where no reaction occurred which indicates that the reaction needs some initiation either by heat or light. Finally, it is concluded that the photochemical oxidation of glucose/fructose by chloramine-T induced by visible light in acidic medium gives formic acid, formaldehyde, CO_2, water and HCl as the reaction products.

References

1. Finar L.L., Organic Chemistry Vol.1: The Fundamental Principles, Sixth Edition **(1973)**

2. Brand Hans, Brand Elzbieta, Goliath Buissness Knowledge on Demand (**2002**)

3. Singh M.P., Singh H.S., Tiwari S.C., Gupta K.C., Singh A.K., Singh V.P. and Singh R.K., Oxidation of D-glucose, D-xylose, D-fructose, L-arabinose and L- sorbose by ammoniacal silver nitrate, *Ind. J. of Chem.* **13,** 819-22, **(1975)**

4. Krupenskii V.I., Oxidation of D-glucose by variable-valence metal ions in acid medium, *Zhurnal Obschii Khimii,* **48,** 2228, **(1978)**

5. Shah M.P., Bromide-catalyzed oxidation of to fructose by cerium (IV) in aqueous H_2SO_4 solution, *J. Ind. Chem. Soc.,* **72, (1995)**

6. Rangappa K.S., Raghavendra M.P., Mahadevappa D.S. and Gowda D.C., Kinetics and mechanism of oxidation of erythro-series pentoses and hexoses by N-chloro-p-toluene sulphonamide, *Carbohydrate Research,* 57-67, **(1998)**

7. Silva E., Edwards A.M. and Pacheco D., Visible light induced photo-oxidation of glucose sensitized by riboflavin, *J. Nutr. Biochem,* **10(3),** 181-5, **(1999)**

8. Prashanth P.A., Mantelingu K., Anandamurthy A.S., Anitha N., Rangaswamy and Rangappa K.S., Kinetics and mechanism of oxidation of hexoses by bromamine-T in alkaline medium, *J. Ind. Chem. Soc.*, **78, (2001)**

9. Bhagwat V.W., Tiwari J. and Pare B., Kinetics and mechanism of cetyltrimethyl ammonium bromide catalyzed oxidation of diethylene glycol by chloramine-T in acidic medium, *J. Serb. Chem. Soc,* **68(7),** 535-542, **(2003)**

10. Buriova E., Medova M., Macasek F. and Bruder P.J., Separation and detection of oxidation products of fluorodeoxyglucose and glucose by high-performance liquid chromatography-electrospray ionization mass spectrometry, *Chromatogr. A* **1034,** 133-137 **(2004)**

11. Rangappa K.S., Oxidation of monosaccharides by N-metallo-N-haloaryl sulphonamide, *J. Ind. Chem. Soc.*, **81, (2004)**

12. Tran H., Chiang K., Scott J. and Amal R., Understanding selective enhancement by silver during photocatalytic oxidation, *Photochem.Photobiol,* **27**, 565, **(2005)**

13. M.N. Rashed and A.A. El-Amin, Photocatalytic degradation of methyl orange in aqueous TiO_2 under different solar irradiation sources, 2(3), 073-081, **(2007)**

14. Singh A.K., Shrivastava S., Srivastava J. and Singh R., Kinetics and mechanism of Ir (III) catalyzed oxidation of xylose and maltose by potassium iodate in aqueous alkaline medium, *Carbohydrate Research,* **(2007)**

15. Pare B., Bhagwat V.W., Fogliani C. and Singh P., *Int. J. Che. Soc.,* **5(1),** 322-332 **(2007)**

16. Singh A.K., Shrivastav J. and Rahmani S., Mechanistic studies of oxidation of D-arabinose and D-mannose by acidic solution of N-bromoacetamide in presence of chloro-complex of Ru(III) as homogenous catalyst, *J. of Molecullar Catalysis A: Chemical,* **271,** 151-160 **(2007)**

17. Bonesi S.M., Fagoni M. and Albini A., Photosensitized electron transfer oxidation of sulfides: structure and medium effect, *J. of sulfur chemistry,* **29,** 367-376 **(2008)**

18. Neppolian ., Celic E and Choi H., Photochemical oxidation of Arsenic (III) to Arsenic (IV) using peroxydisulfate ions as an oxidizing agent, *Enviro. Sci. Technol,* **42(16),** 6179-6184 **(2008)**

19. Brien O., Peter J., Arno S. and Nandita R., *Red Orbit,* **(2008)**

20. Merli D., Profumo A., Dondi D. and Albini A., Photochemical studies of gold electrodes chemically modified with single walled carbon nanotubes., *Chem. Phys. Chem,* **10,** 1090-1096 **(2009)**

21. Singh A.K., Negi R., Jain B., Katre Y., Singh S.P. and Sharma V.K., Kinetics and mechanism of Ru (III) catalyzed oxidation of paracetamol by chloramine-T in aqueous acidic medium, *Catalysis Letters,* **32(1-2)**, 285-291 **(2009)**

22. Sharma V., Sharma K. and Bhagwat V.W., Catalytic effect of cetyltrimethyl ammonium bromide on the oxidation of tetra ethylene glycol by chloramine-T in acetic acid medium, *Asian J. of Chem,* **21(6)**, 465-4274, **(2009)**

23. Zhao Wei, Tong Bin, Zhi Jun-Ge, Pan Yue-Xiu, Shen Jin Bo, Shi Jiang Bing and Dong Gu Ping, *Acta Physico Chimica Sinica,* **26(04),** 822-826 **(2010)**

24. Santhanalakshmi J. and Komalavalli R., Visible Light Induced Photocatalytic Degradation of some Textile Dyes Using Silver Nano Particles, *Res.J.chem.sci.,* **2(4),** 64-67 **(2012)**

25. Diwya, Iyengar Pushpa and Ramachandrappa R., Oxidation of Tranexamic Acid by Bromamine - T in HCl Medium Catalyzed by $RuCl_3$: A Kinetic and Mechanistic Approach, *Res.J.chem.sci.,* **2(7),** 7-15 **(2012)**

26. Chandrashekar, Venkatesha B.M. and Ananda S., Kinetics of Oxidation of Vitamin-B3 (Niacin) by Sodium N-bromo benzenesulphonamide (Bromamine-B) in HCl Medium and Catalysis by Ru(III) ion, *Res.J.chem.sci.,* **2(8),** 26-30 **(2012)**

27. Ghosh Manoj Kumar and Rajput Surendra K., Uncatalysed Oxidation of Dextrose by Cerium(IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Study, *Res. J. Chem. Sci. ,* **2(11),** 55-60**(2012)**

28. Ramasamy Subramanian and Arunachalam Chellamani, Kinetics and Mechanism of (salen)MnIII Catalyzed Oxidation of Aryl phenyl Sulfides with Sodium Metaperiodate, *Res. J. Chem. Sci.,* **3(4),**29-35**(2013)**

29. Sarasan Geetha and Pathak Namrata, Effect of Acetic Acid on Chlorination of some Phenols by Chloramine-T: A Kinetic Approach, *Res.J.chem.sci.,* **4(3),** 86-89, **(2014)**

30. Hine, *Physical organic chemistry,* 132, **(1962)**

31. Gillion R.D., *Introduction to physical organic chemistry*, 168, **(1970)**

32. Deepa D. and Chandramohan G., Kinetic and Mechanistic Study on the Oxidation of Indole-3-Propionic Acid in Acetic Acid Medium *Res. J. Chem. Sci.,* **2(10),** 70-74**(2012)**