Asian Journal of Chemistry Vol. 6, No. 3 (1994), 636–640

Kinetics of Oxidation of Galactose and Mannose with Iodine in Alkaline Media

M.K. SINGH, N. PRASAD AND H.K. SINHA*
P.G. Department of Chemistry
A.M. College, Gaya-823 001, India

The kinetics of oxidation of galactose and mannose with iodine in alkaline media have been investigated at different pH. The results indicate that the active oxidizing species is hypoiodous acid. The maximum oxidation in each case is found around pH 11.20. A first order dependence in hypoiodous acid, in galactose and in mannose has been observed. Change in ionic strength of the medium shows no effect on the reaction rate. A probable mechanism consistent with experimental results has been proposed.

INTRODUCTION

Kinetic investigations of the oxidative reaction involving reducing sugars and iodine in alkaline solution have been reported by many workers[1–7]. The present study aims at getting more information about the oxidation of galactose and mannose with iodine in alkaline media with a view to characterizing the active oxidising species of iodine in aqueous solution of alkaline buffer and proposing a suitable mechanism.

EXPERIMENTAL

Reagents used were (BDH and E. Merck) AR grade samples. Aqeuous solutions of galctose and mannose (Loba) were freshly prepared. For the purpose of present study M/10 solutions by weight of galactose, mannose and iodine (in M/10 potassium iodide) were prepared. The requisite volumes of alkaline buffer solutions[8–10] of desired pH and the substrates were taken in 100 ml conical flasks kept in a thermostat maintained at the desired temperatures. To this was added required volume of iodine solution which too was maintained at the temperature of the reaction. The kinetics of the reaction were followed by removing 5 ml aliquots from the reaction mixture at different intervals of time and the reaction was stopped by adding 50 ml of cold 3% sulphuric acid. The iodine liberated was immediately titrated against 2.50×10^{-3} M sodium thiosulphate solution in the presence of a small amount of sodium bicarbonate. Reproducible results were always obtained.

RESULTS AND DISCUSSION

In order to investigate the dependence of the reaction on hypoidous acid, the reactions were studied at different concentrations of hypoiodous acid (obtained by adding iodine solution to alkaline buffer solutions of varying pH) keeping the concentration of other reactants constant. Oxidizing species-substrate reaction was quite fast in the begining of the reaction. Therefore, the value of the rate of oxidation was determined from the slope of the graph plotted between time of reaction and volume of sodium thiosulphate solution used in all the sets of experiments. The slope gives value of (–dc/dt) in terms of volume of sodium thiosulphate solution consumed per min. The values of K_s was calculated by multiplying –dc/dt by the strength of titrant divided by volume of aliquot taken from the reaction mixture. Table 1 records the results of various experiments at different concentrations of hypoiodous acid. The approximate values of hypoiodous acid are calculated by the following relationship $[I_2] + [HOI] + [IO^-] + I_2$ = total iodine concentrations of I_2 at different pH with following equilibrium constants.

$$K_1 = \frac{[H^+][I^-][HOI]}{I_2} = 3 \times 10^{-13}$$

$$K_2 = \frac{[H^+][OI^-]}{[HOI]} = 10^{-11}$$

and

$$K_3 = \frac{[I_2][I^-]}{[I_3^-]} = 1.36 \times 10^{-3}$$

A close examination of the results of Table 1 indicates that values of K_S vary with the change in concentration of hypoiodous acid. Hence, order of the reaction with respect to hypoiodous acid is unity.

TABLE 1

VARIATION OF K_S WITH [HOI].

temp. = 30°; $[I_2] = 8.50 \times 10^{-3}$ M for [Galactose] = 16.66×10^{-3} M

$[I_2] = 12.50 \times 10^{-3}$ M for [Mannose] = 25.00×10^{-3} M

Galactose			Mannose		
$[HOI] \times 10^4$ (M)	$K_S^* \times 10^5$ ($M\ cm^{-3}\ min^{-1}$)	$K \times 10$ (min^{-1})	$[HOI] \times 10^4$ (M)	$K_S^* \times 10^5$ ($M\ cm^{-3}\ min^{-1}$)	$[HOI] \times 10^4$ (min^{-1})
3.40	6.50	1.91	4.90	9.00	1.84
4.50	8.50	1.90	5.70	10.00	1.80
4.80	9.10	1.90	7.10	13.00	1.83
5.90	11.20	1.90	8.40	15.00	1.80
7.40	14.10	1.90	12.00	21.00	1.75
11.60	22.10	1.90	13.30	23.50	1.80
13.00	24.80	1.90	—	—	—

$K_S^* = -dc/dt \times s/v \times 10^5\ M\ cm^{-3}\ min^{-1}$.

To find out the order with respect to substrate, the reactions were studied at different concentrations of the substrate keeping the concentration of the other reactants constant. The results have been recorded in Table 2.

TABLE 2

VARIATION OF K_s WITH CHANGE IN CONCENTRATION OF SUBSTRATE.

Temp. = 25°; $[I_2] = 4.30 \times 10^{-3}$ M and pH = 9.60 for Galactose.
$[I_2] = 1.20 \times 10^{-3}$ M and pH = 10.10 for Mannose

[Galactose] × 10^2 (M)	$K_s \times 10^5$ (M cm^{-3} min^{-1})	K × 10^2 (min^{-1})	[Mannose] × 10^2 (M)	$K_s \times 10^5$ (M cm^{-3} min^{-1})	K × 10^2 (min^{-1})
0.87	4.50	0.52	2.50	1.08	0.43
1.70	8.60	0.50	5.00	2.30	0.46
2.61	12.00	0.46	10.00	3.80	0.38
3.48	17.00	0.49	15.00	5.95	0.39
4.35	20.50	0.47	20.00	6.90	0.35

The results indicate that the values of K_s is directly proportional to the concentration of the substrates (galactose and mannose) and hence order of the reaction with respect to substrates is unity because the values of first order velocity constant are fairly constant.

The effect of pH on the rate of oxidation was studied and it was observed that at pH below 11 and above 12, the rate of oxidation was unaffected as evident from Table 3. The maximum oxidation takes place in the vicinity of pH 11.20.

TABLE 3

VARIATION OF K_s WITH pH.

Temp. = 30°; $[I_2] = 8.50 \times 10^{-3}$ M for [Galactose] = 16.66×10^{-3} M
$[I_2] = 12.50 \times 10^{-3}$ M for [Mannose] = 25.00×10^{-3} M

Galactose		Mannose	
pH	$K_s \times 10^5$ (M cm^{-3} min^{-1})	pH	$K_s \times 10^5$ (M cm^{-3} min^{-1})
10.10	6.50	10.00	9.00
10.80	8.50	10.30	10.00
11.00	9.10	11.20	23.50
11.30	24.80	11.40	21.00
11.80	22.10	11.90	15.00
12.20	14.10	12.20	13.00
12.30	11.20	—	—

The plot of rate of oxidation *versus* pH was found to be identical with the plot of [HOI] versus pH. From these plots it has been concluded that active oxidizing species is hypoiodous acid and both the sugars follow the same kinetic path.

With galactose and mannose, the effect of adding varying amounts of KCl to the reaction mixture was examined, but no appreciable salt effect was detected. The absence of salt effect demonstrates that the reaction does not take place between ionic substances. Hence at least one of the reactants must be non-ionic and this is also conformed[11] by the activation energy of galactose and mannose (Table 4).

TABLE 4

VARIATION OF K_s WITH TEMPERATURE.

$[\text{Substrate}] = 25.00 \times 10^{-3}$ M; $[I_2] = 12.50 \times 10^{-3}$ M; pH = 9.40 (Galactose); pH = 11.90 (Mannose)

Galactose				annose			
Temp. (°C)	$1/T \times 10^4$	$K_s \times 10^5$ ($M\ min^{-1}$)	Ea (Kcal/mol)	Temp. (°C)	$1/T \times 10^4$	$K_s \times 10^5$ ($M\ min^{-1}$)	Ea (Kcal/mol)
25	33.56	8.50		25	33.56	13.50	
30	33.02	14.00		30	33.02	18.00	11.82
35	32.46	17.00	12.50	35	35.46	26.00	
40	31.97	21.00		40	31.97	—	

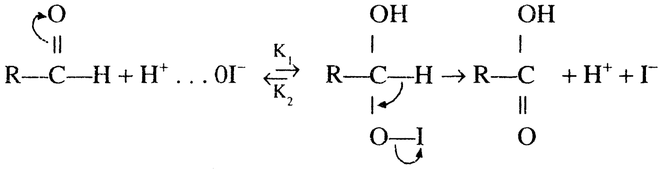
These results confirm that the reaction takes place between substrate (galactose and mannose) and hypoiodous acid.

The value of equivalence for the oxidation of galctose and mannose by iodine in alkaline solution is approximately unity in each case and the reaction products have been confirmed by paper chromatography.

From the above observations the following mechanism of the oxidation of galactose and mannose by iodine in alkaline solution may be suggested:

(i) $I_2 + H_2O \rightleftharpoons H^+ + I^- + HOI$

(ii)



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + H^+ \ldots OI^- \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R{-}\underset{\underset{\displaystyle O{-}I}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}H \rightarrow R{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle OH}{|}}{C}} + H^+ + I^-$$

R = carbohydrate chain.

The above reaction mechanism leads to the following rate expression:

$$\text{Rate} = \frac{-d[HOI]}{dt} = K[RCHO][HOI]_T$$

where $[HOI]_T = [HOI] + [HOI]_{complex}$.

REFERENCES

1. P.D. Bartlett, *J. Am. Chem. Soc.*, **56,** 967 (1934); O.G. Ingles and G.C. Israel *J. Chem. soc.*, 810 (1948), 1282 (1950).
2. B.A. Marshall and W.A. Waters, *J. Chem. Soc.*, 1581 (1961).
3. N. Bhattacharya and M.L. Sen Gupta, *Indian J. Chem.* **15A,** 573 (1977).
4. M.C. Sanhed, Comprehensive Inorganic Chemistry, Van Nostrand, London, Vol. 3, p. 91, (1954); F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, New Delhi, p. 567 (1970).
5. Z. Furth, *Elektrochem.*, **28,** 57 (1922); W. Bray, *J.Am. Chem. Soc.*, **33,** 932 (1911); Jakowkin, *Z. Phys. Chem.*, **13,** 539 (1894).

6. H.M. Judd, *Biochem. J.*, **14,** 255. (1920).
7. M. Macleod and R. Robinson, *Biochem. J.*, **23,** 519 (1929).
8. I.M. Kolthoff, *J. Biol. Chem.*, **23,** 135 (1935).
9. Kolthoff and Vluschhouwer, *Bio. chem. Z.*, **189,** 191 (1927).
10. ________,*Chem. Weekblad,* **24,** 526 (1927).
11. Mahesh, C. Agrawal, *J. Chem. Soc., Perkin II* 762 (1973).

[*Received:* 30 January 1993; *Accepted:* 4 October 1993] AJC-705