Mechanism of Oxidation of Aldoses by Chloramine T

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The kinetics of the oxidation of four aldoses, xylose, arabinose, mannose, and galactose have been investigated in highly alkaline media. The reactions show a brief initial induction period after which first-order dependence on both chloramine T, and the aldose follows. The order in hydroxide ions has been found to be second but shows a slight decrease at high concentration of alkali. The energies of activation have been obtained as 22—23·8 and 28—30 kcal mol^{-1} for the oxidation of pentoses and hexoses respectively. A mechanism involving a termolecular rate-determining reaction among hypochlorite ion, hydroxide ion, and the anion derived from the β-anomer of aldose is suggested. The oxidation rates follow the order xylose > arabinose > galactose > mannose.

THE oxidation of aldoses has been studied in detail by using halogens as the oxidising agents. Isbell and his co-workers [1] pioneered studies on the oxidation of aldoses by bromine and found the corresponding aldonic acids as the primary products of oxidation. The work also showed that β-aldoses [C(1) equatorial] are oxidised much faster than α-aldoses [C(1) axial]. For several pentoses and hexoses, Barker and his co-workers [2] have suggested that oxidation takes place predominantly after rate-determining anomerisation to the β-form.

The oxidation of aldoses by chlorine,[3] bromine,[4] and iodine [5] has been reported in alkaline media. Hypochlorous, hypobromous, and hypiodous acids were established as the main oxidising species. All these investigations revealed the faster rate of oxidation of pentoses than hexoses.[6]

It was observed that the oxidation of aldoses by chloramine T takes place only in highly alkaline solutions. In this paper, kinetic results of the oxidation of xylose, arabinose, mannose, and galactose are reported and a mechanism suggested.

EXPERIMENTAL

Aqueous solutions of L-arabinose (Merck), (+)-D-xylose (Merck), (+)-D-galactose (Merck), and (+)-D-mannose (Baker) were freshly prepared. Stock solutions of chloramine T and sodium hydroxide were prepared from Merck proanalysi samples in doubly distilled water. All other reagents used were of analytical grade and stills employed were of Jena glass.

The kinetics were followed by examining aliquot portions of the reaction mixture for chloramine T by iodometry using starch indicator. The alkali–aldose mixture was allowed to equilibrate for exactly 30 min, after which chloramine T was added to start the reaction.

RESULTS

The oxidation of aldoses by chloramine T was investigated at several initial concentrations of the reactants. It was observed that the reactions show an initial induction period after which first-order dependence on chloramine T follows. Pseudo-first-order constants (k_1) in chloramine T were calculated from the slope of the straight line portions of the log k_1–time plots which showed a uniform increase with increase in aldose concentration (Table 1).

The reactions, therefore, have first-order dependence on aldose, and the average second-order rate constants ($k_2 = k_1$/[Aldose]) have been calculated as 9·6 ± 0·3, 19·8 ± 1·2, 14·2 ± 0·3, and 12·0 ± 1·0 × 10^{-3} l mol^{-1} s^{-1} for the oxidation of arabinose, xylose, mannose, and galactose respectively under the conditions of Table 1. The slight decrease observed in first-order rate constants at high

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[1] H. S. Isbell, *J. Res. Bur. Stand.*, 1932, **8**, 615; 1937, **18**, 505; 1937, **18**, 141; *J. Amer. Chem. Soc.*, 1932, **54**, 1692; 1933, **55**, 2166.

[2] I. R. L. Barker, W. G. Overend, and C. W. Rees, *Chem. and Ind.*, 1960, 1297.

[3] E. A. Shilov and A. A. Yasnikov, *Ukrain. khim. Zhur.*, 1967, **5**, 595.

[4] N. Bhattacharya and M. L. Sen Gupta, *Indian J. Chem.*, 1967, **5**, 554.

[5] O. G. Ingles and G. C. Israel, *J. Chem. Soc.*, 1948, 810.

[6] B. Capon, *Chem. Rev.*, 1969, **69**, 407.

TABLE 1

Effect of concentration of reactants at 45°

Expt. no.	10^3[Chloramine T]/ M	10^2[Aldose]/ M	10^5k_1/s^{-1} Arabinose [a]	Xylose [a]	Mannose [b]	Galactose [c]
1	1·2	2·0	14·4		30·7	23·0
2	1·6	2·0	15·1	42·2	30·7	23·2
3	2·0	2·0	16·9	42·2	30·0	23·0
4	2·8	2·0	12·6	32·2	28·0	20·1
5	4·0	2·0	11·9	29·0	25·0	19·2
6	2·0	1·2	11·5	27·9	16·0	13·4
7	2·0	1·6	14·1	34·2	21·9	18·4
8	2·0	2·8	26·3	48·0	41·5	33·0
9	2·0	4·0	34·7	64·5	57·6	52·2

[a] In presence of 0·02M-NaOH. [b] In the presence of 0·10M-NaOH. [c] In the presence of 0·05M-NaOH.

chloramine T concentrations may be attributed to the deactivation caused by the formation of small amounts of $NaClO_3$ in a side reaction as suggested earlier.[7,8]

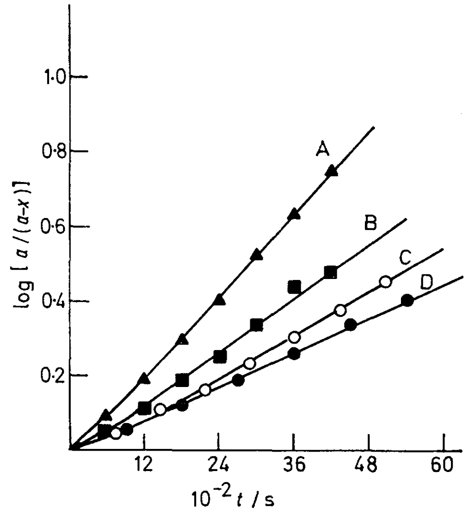

FIGURE 1 First-order rate plots at 45°, conditions as in experiment no. 3 of Table 1: A, xylose; B, mannose; C, galactose; D, arabinose

The most interesting feature of the oxidation of aldoses by chloramine T is the dependence of alkali on the rate of oxidation. The results show that the reactions are highly susceptible to a change in alkalinity (Tables 2 and 3).

TABLE 2

Dependence of rate on hydroxide ion concentration [a]

10^2[OH$^-$]/M	10^5k_1/s^{-1} Arabinose 40°	Arabinose 45°	Xylose 40°	Xylose 45°
1·2	5·43	14·0	9·10	23·2
1·6	8·89	19·2	16·0	36·5
2·0	14·4	29·5	27·0	51·0
2·8	23·6	47·2	45·0	76·8
4·0	43·2	76·8	83·3	140

[a] [Chloramine T] = 2·0 × 10^{-3}M, [Aldose] = 2·0 × 10^{-2}M, [$NaClO_4$] = 0·2M.

The order of reaction in hydroxide ions was calculated from the slope of the plots of log k_1 vs. log[OH$^-$] (Figure 2). It was observed that the reactions have second-order dependence on hydroxide ions at lower alkali concentrations while at higher concentrations the order decreases.

The effect of neutral salts, *e.g.* $NaClO_4$, KCl, and NaCl was investigated. The results (Tables 4—6) show that the oxidation of aldoses by chloramine T exhibits a positive salt effect.

TABLE 3

Dependence of rate on hydroxide ion concentration

10^2[OH$^-$]/ M	10^5k_1/s^{-1} Mannose [a] 40°	45°	10^2[OH$^-$]/ M	10^5k_1/s^{-1} Galactose [b] 40°	4*t*°
6·0	15·3	28·7	3·0	11·2	20·3
8·0	29·2	48·0	4·0	18·2	34·9
10·0	37·4	72·9	5·0	27·4	50·4
14·0	46·1	104	7·0	42·6	76·8
18·0	66·8		10·0	74·8	147
20·0		180			

[a] [Chloroamine T] = 2·0 × 10^{-3}M, [Aldose] = 2·0 × 10^{-2}M, [$NaClO_4$] = 0·8M. [b] [Chloroamine T] = 2·0 × 10^{-3}M, [Aldose] = 2·0 × 10^{-2}M, [$NaClO_4$] = 0·4M.

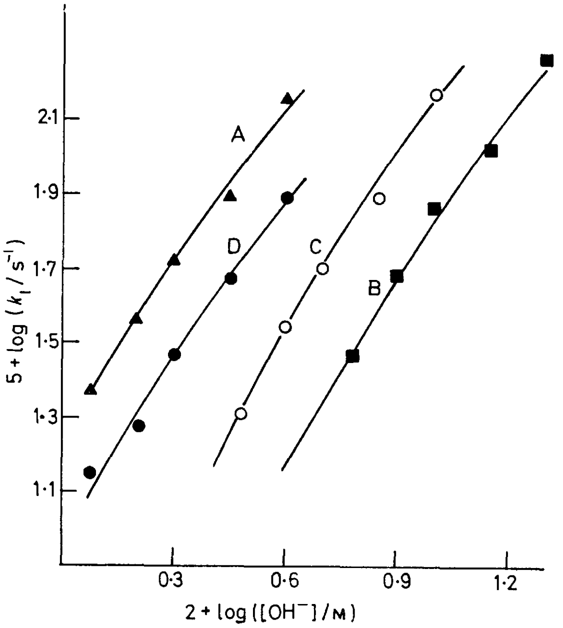

FIGURE 2 Plot of log k_1 against log [OH$^-$] at 45°, conditions as in Tables 2 and 3: A, xylose; B, mannose; C, galactose; D, arabinose

The influence of several other factors on the rate of oxidation of aldoses by chloramine T was also studied. The effect of addition of methanol (5—25%) was negligible.

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[7] B. Singh and A. Rehman, *J. Indian Chem. Soc.*, 1940, **17**, 169.

[8] S. P. Mushran and M. C. Agrawal, *J. Chem. Soc.* (*B*), 1971, 1712.

TABLE 4

Effect of addition of sodium perchlorate at 40° *

[NaClO$_4$]/M	10^5k_1/s^{-1} Arabinose	10^5k_1/s^{-1} Xylose	[NaClO$_4$]/M	10^5k_1/s^{-1} Mannose	[NaClO$_4$]/M	10^5k_1/s^{-1} Galactose
	8·30			14·5		14·1
0·02	9·02	22·0	0·24	20·0	0·12	15·7
0·04	9·66	22·7	0·32	21·9	0·16	18·0
0·08	11·5	23·4	0·40	25·6	0·20	21·0
0·12	12·0	24·6	0·56	31·2	0·28	24·8
0·20	14·4	27·0	0·80	37·4	0·40	27·4

* Concentration of alkali as in Table 1. Concentration of reactants, as in Table 2.

TABLE 5

Effect of addition of potassium chloride at 40° *

[KCl]/M	10^5k_1/s^{-1} Arabinose	10^5k_1/s^{-1} Xylose	[KCl]/M	10^5k_1/s^{-1} Mannose	10^5k_1/s^{-1} Galactose
	8·30			14·5	14·1
0·04	9·60	26·4	0·08		15·7
0·08	11·3	30·1	0·16		17·6
0·12	13·1	30·7	0·24	19·2	21·2
0·20		33·5	0·40	27·2	26·1
0·22	13·7		0·56	31·2	
			0·80	36·8	

* Conditions as in Table 4.

TABLE 6

Effect of addition of sodium chloride at 40° *

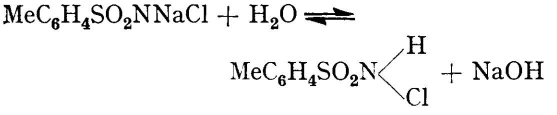
[NaClO$_4$]/M	10^5k_1/s^{-1} Arabinose	10^5k_1/s^{-1} Xylose	[NaClO$_4$]/M	10^5k_1/s^{-1} Mannose	[NaClO$_4$]/M	10^5k_1/s^{-1} Galactose
	8·30			14·5		14·1
0·04	9·60	27·7	0·12	16·6	0·06	15·7
0·06	11·1		0·20	18·9	0·10	18·8
0·08		30·1	0·28	22·8	0·14	21·4
0·10	12·2		0·40	25·3	0·20	24·0
0·14		34·5	0·60	31·5	0·30	31·1
0·20	14·5	37·0				

* Conditions as in Table 4.

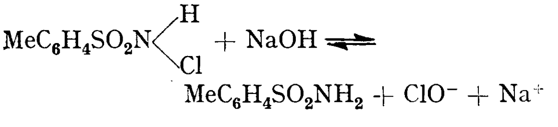
Unlike the oxidation of α-hydroxy-acids,[8] osmium(VIII) ions were found to be inactive as catalysts of the rate of oxidation. The effect of temperature was quite marked and from the values of the rate constants at 40, 45, 50, and 55°, the Arrhenius activation energies were calculated as 23·0 ± 0·3, 21·9 ± 0·2, 28·8 ± 0·2, and 29·4 ± 0·3 kcal mol⁻ for the oxidation of arabinose, xylose, mannose, and galactose respectivity.

DISCUSSION

The results of the oxidation of arabinose, xylose, mannose, and galactose, recorded here, have revealed that the reactions have identical kinetics and thus appear to have a common mechanism. It is well known that the hydrolysis of chloramine T in alkaline solutions involves the steps (1a) and (1b).[9]

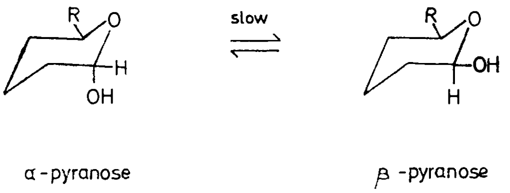


$$\mathrm{MeC_6H_4SO_2NNaCl + H_2O \rightleftharpoons MeC_6H_4SO_2N{<}^{H}_{Cl} + NaOH} \quad (1a)$$

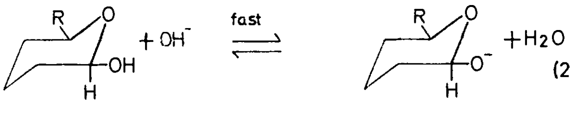


$$\mathrm{MeC_6H_4SO_2N{<}^{H}_{Cl} + NaOH \rightleftharpoons MeC_6H_4SO_2NH_2 + ClO^- + Na^+} \quad (1b)$$

N-Chlorotoluene-*p*-sulphonamide as an oxidising species has been suggested for acid-catalysed reactions[10] only. In highly alkaline media the favoured species



(2a)



(2b)

would be hypochlorite ion and thus should be responsible for the oxidative action of chloramine T.

Further, aldoses in alkaline solutions exist as anions

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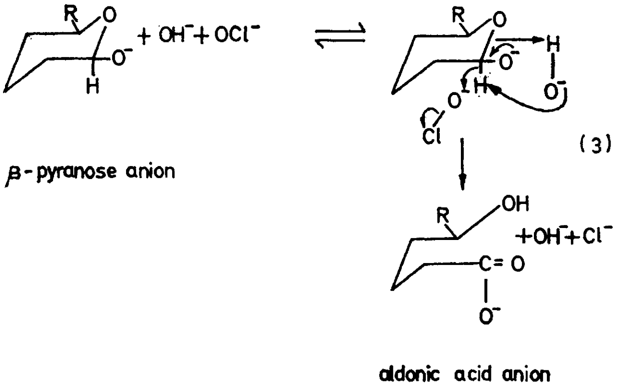
[9] R. Dietzel and K. Taufel, *Apotheker Ztg.*, 1929, **44**, 989.

[10] M. C. Agrawal and S. P. Mushran, *J. Phys. Chem.*, 1971, **75**, 838.

derived from their β-anomers[11,12] and accordingly steps (2a) and (2b) are involved, where R represents H or CH_2OH for a pentose and hexose respectively. The anomerisation step (2a) is slow[11] and therefore restricts the formation of aldose anion [step (2b)].

The first-order dependence of the reaction rate on chloramine T and aldose and a second-order dependence on hydroxide ion suggests that the rate-determining step during the oxidation of aldoses involves the anion of aldose, hypochlorite ion, and hydroxide ion. The C(1)–H bond is probably ruptured during the formation of the open chain aldonic acid anion [process (3)].



(3)

The mechanism of oxidation of aldoses (S) may be summarised by equations (4)—(6). Step (5) is slow but not as slow as the rate-determining step (6). On adding sugar to the alkali solution, the concentration of aldose anion S^- increases with time. When $[S^-]$ becomes sufficiently high, the consumption of S^- in step (6) becomes regular and a steady state is achieved. Thus the steady state in the oxidation of aldoses is not achieved instantaneously; this has also been observed from the first-order rate plots which show an induction period (Figure 1). The steady state is reached in <0·5 h at 45° and even more quickly at higher temperatures.

$$MeC_6H_4SO_2NNaCl + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MeC_6H_4SO_2NH_2 + ClO^- + Na^+ \quad \text{fast} \quad (4)$$

$$S + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S^- + H_2O \quad \text{slow} \quad (5)$$

$$S^- + OH^- + OCl^- \xrightarrow{k_3} \text{Products} \quad \text{slowest and rate determining} \quad (6)$$

Applying steady-state conditions to $[S^-]$, the rate of disappearance of hypochlorite is given by equation (7).

$$d[ClO^-]/dt = \frac{k_2k_3[S][ClO^-][OH^-]^2}{k_{-2}[H_2O] + k_3[ClO^-][OH^-]} \quad (7)$$

The iodometric titre value for the reaction mixture corresponds to both chloramine T and hypochlorite and chloramine T is consumed only in the formation of hypochlorite. Thus equation (8) is obtained.

$$d[\text{chloramine T}]/dt = \frac{k_2k_3[S][ClO^-][OH^-]^2}{k_{-2}[H_2O] + k_3[ClO^-][OH^-]} \quad (8)$$

According to the rate law the rate of oxidation of aldoses by chloramine T will follow a first-order dependence on aldose and chloramine T and a second-order dependence on $[OH^-]$ when $k_{-2}[H_2O] \gg k_3[ClO^-][OH^-]$. k_{-2} Is fairly large and k_3 is small, being the constant for the rate-determining step, and thus the above approximation will be valid for low concentrations of hydroxide ion and the order in alkali will be two. At higher alkali concentrations the approximation will not strictly hold and the order in alkali will decrease. The experimental results (Figure 2) show a decrease in order with respect to alkali at higher concentrations of NaOH and are, therefore, consistent with the rate law (8).

The rate-determining step (6) involves an interaction between three similarly charged ions which would require a very high energy of activation. In fact, the activation energies have been found to be quite large, 22—23·4 kcal mol^{-1} for the pentoses and 28—30 kcal mol^{-1} for the hexoses. The reactions have been observed to be quite slow and base catalysed and thus support the rate-determining step (6). A positive salt effect is also consistent with a rate-determining reaction involving similarly charged ions.

The stoicheiometry of the reactions was also determined. It was observed that equivalent amounts of reactants were consumed and that the corresponding aldonic acids were formed.

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[11] I. R. L. Barker, W. G. Overend, and C. W. Rees, *Chem. and Ind.*, 1960, 1298.

[12] B. Perlmutter-Hayman and A. Perskey. *J. Amer. Chem. Soc.*, 1960, **82**, 276.