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KINETICS AND MECHANISM OF OXIDATION OF SOME ALDOSES BY CHROMIC ACID IN PERCHLORIC ACID MEDIUM

KALYAN KALI SEN GUPTA*, SHIPRA SEN GUPTA, AND SAMARENDRA NATH BASU
Department of Chemistry, Jadavpur University, Calcutta-700032 (India)
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ABSTRACT

The kinetics of chromic acid oxidation of D-galactose, D-mannose, L-arabinose, and D-xylose have been studied in perchloric acid media. The reactions show first-order dependence on both chromium(VI) and aldose concentrations. The order with respect to hydrogen-ion concentration in each reaction is complex, and the hypotheses for the mechanism of acid catalysis have been tested. Different activation parameters have been evaluated. Aldoses are oxidized mainly to the aldonic acids when the aldose substrate is in excess. A tentative reaction mechanism has been suggested.

INTRODUCTION

The oxidation of some aldoses by halogens and chloramine T has been studied in alkaline medium[1-4]. Although some work on the kinetics of oxidation of aldoses has also been carried out[5-9] in acid medium, no systematic kinetic study of the oxidation of aldoses by chromic acid in perchloric acid and its mechanism has been reported. Moreover, it is well known that the products of oxidation of aldoses depend on the nature of the oxidant used. Thus, the mild oxidant bromine yields aldonic acids, whereas the stronger oxidant nitric acid yields aldaric acids; nothing is conclusively known about the product of oxidation by chromic acid in perchloric acid media. We now report on the kinetics and mechanism of chromic acid oxidations in perchloric acid.

MATERIALS AND METHODS

Reagents. — All of the materials employed were of the highest purity available. D-Xylose, L-arabinose, D-mannose, and D-galactose were E. Merck products. Aqueous solutions of the aldoses were freshly prepared in doubly distilled water. Potassium dichromate (G.R., E. Merck) was used. Solutions of perchloric acid were made from a Merck proanalysi sample and concentration was expressed in molarity.

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*To whom correspondence should be sent.

Kinetic measurements — The rate of disappearance of chromium(VI) was followed spectrophotometrically at 350 nm with a Beckman DU model spectrophotometer, using a cell of path-length 1 cm The spectrophotometer was fitted with a cell compartment that was kept at constant temperature All the substrates are transparent at this wavelength, and neither chromium(III) nor the oxidized products has any appreciable absorption at this wavelength. Reaction was initiated by mixing the requisite quantity of the substrate, maintained at the desired temperature, with the solution of chromium(VI) and perchloric acid The reactions were followed for at least 65, 70, 55, and 50% conversion of the initial chromium(VI) for the oxidations of galactose, mannose, arabinose, and xylose, respectively. The conversion was much greater at higher concentrations of substrate and higher temperatures Generally, 6–8 experimental points were noted in each run The pseudo-first-order rate constants, k_{obs} (in sec^{-1}), were calculated from the plots of log A (absorbance) *vs* time, which were reproducible to within ±5%

Stoichiometry — The reaction mixture containing the substrate and perchloric acid was kept mixed with a large excess of the oxidant for several days at 35° The unconsumed oxidant was then estimated iodometrically The consumption ratio, *i e*, the number of moles of dichromate consumed per mole of aldose, was calculated by assuming that the aldose was totally consumed under these conditions The observed stoichiometry in the presence of a large excess of oxidant (Table I) indicates that chromium(VI) ultimately effects the oxidation of the aldoses to formic acid and carbon dioxide, according to the general equation·

$$C_nH_{2n}O_n + (2n - 1)O \rightarrow HCO_2H + (n - 1)CO_2 + (n - 1)H_2O$$

The above findings are in agreement with the observation by Malangeau and Guernet[9] on the oxidation of aldoses by a large excess of vanadium(V) in acid medium However, throughout the kinetic investigations, the organic substrates were used in an excess sufficiently large to ensure that the rate of reduction of the chromic acid is proportional to the rate of oxidation of the substrates only Moreover, since the initial rate of consumption of chromic acid was always first order

TABLE I

STOICHIOMETRY OF THE OXIDATION OF ALDOSES BY CHROMIUM(VI) IN THE PRESENCE OF A LARGE EXCESS OF OXIDANT

Aldose	*Consumption ratio*		
	Experimentally observed	*On the basis of formic acid formation*	*On the basis of carbon dioxide formation*
D-Galactose	3 7	2 0	4 0
D-Mannose	3 5	2 0	4 0
L-Arabinose	3 2	1 7	3 3
D-Xylose	3 1	1 7	3 3

under these conditions, the rate of oxidation of the intermediate products cannot be kinetically significant[10]

Product analysis — The aldoses were oxidised separately by chromic acid under the kinetic conditions After purification and concentration, the products were identified by paper chromatography (p c) in comparison with the oxidation products of the respective aldoses by bromine and nitric acid separately P c was effected by the descending method with Whatman No 1 paper, 1-butanol–acetic acid–water (4 1 5, upper layer), and detection by alkaline silver nitrate P c of the syrup obtained by oxidation of aldoses with chromic acid indicated the presence of aldonic acids and the corresponding δ- and γ-lactones This is in agreement with the observation[6 11] that the aldonic acid invariably remains in equilibrium with the corresponding δ- and γ-lactones in acid medium

RESULTS

Effect of reactant concentrations The pseudo-first-order rate constants were calculated at different initial concentrations of chromium(VI), but at constant [Aldose] and [$HClO_4$]. The summary of pseudo-first-order rate constants (k_{obs}) in Table II indicates that they are independent of the initial [Chromium(VI)] This suggests that $HCrO_4^-$ or its protonated form is the reactive species of chromium[12]. In another set of experiments, the pseudo-first-order rate constants were measured at different [Aldose], but at constant [Chromium(VI)], [$HClO_4$], and temperature The results presented in Table III show that the reactions are first order with respect to both [Aldopentose] and [Aldohexose] The average second-order rate constants have been computed to be (3 40 ±0 1) × 10^{-1}, (2 02 ±0 1) × 10^{-1}, (6 63 ±0 3) × 10^{-1}, and (3 73 ±0 2) × 10^{-1} l mol^{-1} sec^{-1} for the oxidations of galactose, mannose, xylose, and arabinose, respectively The oxidation rates, therefore, follow the order xylose > arabinose > galactose > mannose This finding is in agreement with the observations of Agrawal *et al*[4]

Effect of perchloric acid concentration The effect of acidity at constant ionic strength (μ = 2 4M) on the pseudo-first-order rate constants was measured The rate

TABLE II

EFFECT OF INITIAL CHROMIUM(VI) CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANT[a]

Aldose	*[Cr(VI)]* × *10^4* M	k_{obs} × *10^4* *(s^{-1})*
D-Galactose	0 55–3 33	5 8 ±0 2
D-Mannose	0 55–3 85	3 1 ±0 1
L-Arabinose	0 55–3 33	6 4 ±0 2
D-Xylose	0 55–2 75	11 5 ±0 5

[a][Aldose] = 1 5mM [$HClO_4$] = 2 4M Temperature, 35°

TABLE III

EFFECT OF SUBSTRATE CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANTS[a]

Rate constant	[Substrate] × 10^3 (M)					
	0 5	1 0	2 0	3 0	4 0	5 0
D-*Galactose*						
$k_{obs} \times 10^4$ (sec^{-1})	1 7	3 4	7 0	10 4	13 6	17 5
$\frac{k_{obs}}{[\text{Substrate}]} \times 10$ (l mol^{-1} sec^{-1})	3 4	3 4	3 5	3 46	3 4	3 5
D-*Mannose*						
$k_{obs} \times 10^4$ (sec^{-1})	1 05	2 14	4 1	5 9	7 9	10 1
$\frac{k_{obs}}{[\text{Substrate}]} \times 10$ (l mol^{-1} sec^{-1})	2 1	2 14	2 05	1 97	1 97	2 02
L-*Arabinose*						
$k_{obs} \times 10^4$ (sec^{-1})	1 86	3 7	7 3	11 2	15 2	19 1
$\frac{k_{obs}}{[\text{Substrate}]} \times 10$ (l mol^{-1} sec^{-1})	3 72	3 7	3 65	3 73	3 8	3 82
D-*Xylose*						
$k_{obs} \times 10^4$ (sec^{-1})	3 4	6 6	13 2	20 7	26 6	33 7
$\frac{k_{obs}}{[\text{Substrate}]} \times 10$ (l mol^{-1} sec^{-1})	6 8	6 6	6 6	6 9	6 65	6 74

[a] [Cr(VI)] = 167μM [HClO$_4$] = 2 4M Temperature, 35°

TABLE IV

SLOPES OF THE ZUCKER–HAMMETT PLOTS

Zucker–Hammett plots	D-*Galactose*	D-*Mannose*	L-*Arabinose*	D-*Xylose*
log k_{obs} *vs* log [HClO$_4$]	2 3	2 5	2 6	2 3
log k_{obs} *vs* $-H_0$	1 6	1 5	1 3	1 3

of oxidation of the aldoses increased with the increase in acid concentration (Fig 1) In an attempt to correlate the oxidation with acid concentration, two hypotheses for the mechanism of acid catalysis were tested The Zucker–Hammett plots[13], *e g* , log $k_{c's}$ against log[HClO$_4$] or log k_{obs} against $-H_0$, are linear, indicating that these reactions are acid-catalysed A summary of the slopes of the Zucker–Hammett plots is given in Table IV The values of the Hammett acidity functions ($-H_0$) at different acidities are those reported by Paul and Long[14]

Effect of Mn^{2+} concentration. The rate of oxidation of the aldoses by chromic acid was studied in the presence of Mn^{2+} ions. The pseudo-first-order rate constant

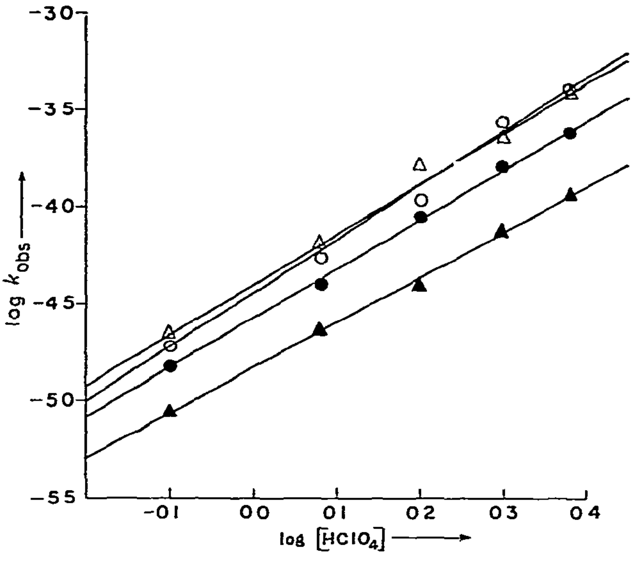


Fig 1 Dependence of pseudo-first-order rate constant on concentration of perchloric acid [Cr(VI)] = 167μM, μ = 2 4M, temperature, 35°, [Aldose] = mM —○—, D-Galactose, —●— D-mannose, —△—, L-arabinose, and —▲—, D-xylose

(k_{obs}) decreased to ~25% and 33% of that in the absence of Mn^{2+} ions in the oxidations of aldohexoses and aldopentoses, respectively No significant decrease in the rate constant was observed with $[Mn^{2+}] \geqslant 2\,0 \times 10^{-2}$M and $6\,2 \times 10^{-3}$M for the oxidations of aldohexoses and aldopentoses, respectively The addition of $NaClO_4$ of the same strength as that of Mn^{2+} ions did not influence the rate of oxidation The results indicate that Mn^{2+} ion catalyses the disproportionation of the intermediate valence states of chromium[15-17]

Influence of temperature and activation parameters The second-order rate constants (k_2) for the oxidations of aldoses at different temperatures were calculated from the relation $k_2 = k_{obs}/[\text{Aldose}]$ The plots of log k_2 against 1/T are linear The Arrhenius activation energies (E_a) have been calculated from the slopes of log k_2 *vs* 1/T plots (Fig. 2) for the oxidations of aldohexoses and aldopentoses The values follow the order E_a (aldohexose) > E_a (aldopentose), and this is in keeping with the result obtained by other workers[4] The enthalpy of activation ($\Delta H^{\ddagger}$) was calculated from the activation energy The entropy of activation ($\Delta S^{\ddagger}$) in each reaction was then evaluated by equating the experimentally obtained values of PZ (l mol^{-1} sec^{-1}) to

$$e^2\left(\frac{kT}{h}\right)e^{\Delta S^{\ddagger}/R}$$

The values of $\Delta G^{\ddagger}$ have been calculated at 303K from the relation $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ The activation parameters are recorded in Table V The negative entropies of activation ($\Delta S^{\ddagger}$) indicate that the reactions occur between ions of similar charge[18]

TABLE V

ACTIVATION PARAMETERS FOR THE OXIDATIONS OF ALDOSES BY CHROMIC ACID IN PERCHLORIC ACID MEDIUM

Aldose	E_a *(kJ mol^{-1})*	$\Delta H^{\ddagger}$ *(kJ mol^{-1} at 303K)*	*log PZ (l mol^{-1} sec^{-1} at 303K)*	$\Delta S^{\ddagger}$ *(J deg^{-1} mol^{-1} at 303K)*	$\Delta G^{\ddagger}$ *(kJ mol^{-1} at 303K)*
D-Galactose	75 ±4	72 ±4	12 23 ±0 72	27 6 ±13	80 ±0 2
D-Mannose	64 ±5	61 ±5	10 01 ±0 93	70 5 ±16	82 ±0 5
L-Arabinose	48 ±3 5	46 ±3 5	7 76 ±0 62	114 ±13	80 ±0 4
D-Xylose	56 5 ±2	54 ±2	8 41 ±0 51	101 ± 9	84 ±0 5

DISCUSSION

The reactions of aldopentoses and aldohexoses, which are similar in character, are first order with respect to the oxidant as well as to the organic reductant, but the order with respect to the acid is complex (2 3–2 8) The latter order can be explained by considering that H_2CrO_4 and H^+CrO_3 are formed[19] successively according to equations *1* and *2*, respectively Moreover, the aldohexoses and aldopentoses are known to exist mainly in the cyclic hemiacetal form Although the ring oxygen

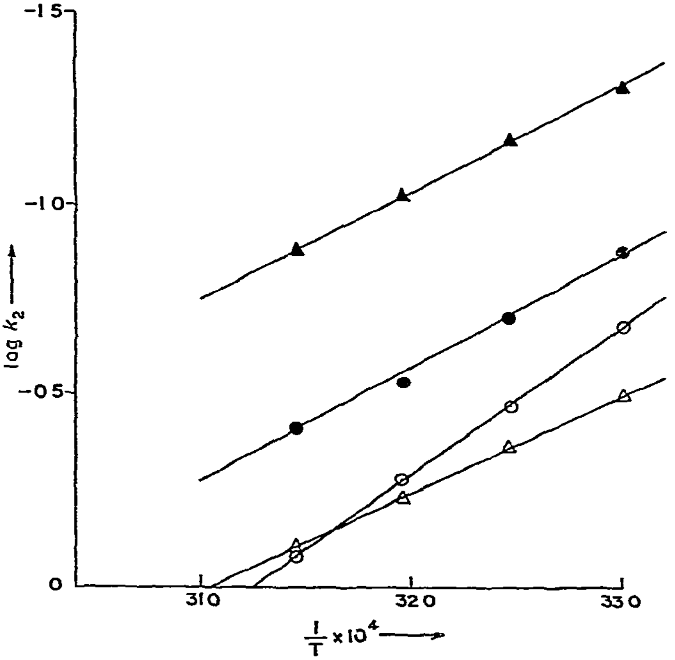


Fig 2 Variation of second-order rate constant with temperature· [Cr(VI)] = 167μM, [Aldose] = mM, and [$HClO_4$] = 2 4M —○—, D-Galactose, —●—, D-mannose, —△—, L-arabinose, and —▲—, D-xylose

atom of the aldoses is less basic than the oxygen atom of ethers[20a] ($pK_{BH^+} = -3\,0$ to $-4\,0$), they are considered to be hard bases[20b] according to Pearson's hard and soft acid–base theory Hence, a rapid and reversible transfer of H^+ to the ring oxygen atom of the aldoses would occur in strong acid The higher order in acid (>2) may be due to the involvement of the protonated aldoses[21] in the reactions The steps of the reactions are as follows·

$$HCrO_4^- + H^+ \overset{K_1}{\rightleftharpoons} H_2CrO_4, \tag{1}$$

$$H_2CrO_4 + H^+ \overset{K_2}{\rightleftharpoons} H^+CrO_3 + H_2O, \tag{2}$$

$$S + H^+ \overset{K_3}{\rightleftharpoons} SH^+ \tag{3}$$

and

$$SH^+ + H^+CrO_3 \xrightarrow[\text{slow}]{k'} P^* + H_2CrO_3, \tag{4}$$

where S, SH^+, and P^* are the organic substrate (*i e* , aldose), its protonated species, and the oxidised product, respectively

The rate expression is

$$V = k'[SH^+][H^+CrO_3] \tag{5}$$

From equations *1* and *2*,

$$[H^+CrO_3] = K_1\,K_2[HCrO_4^-][H^+]^2 \tag{6}$$

From equation *3*,

$$[SH^+] = \frac{K_3[S]_T[H^+]}{1 + K_3[H^+]}, \tag{7}$$

where $[SH^+]$ = the concentration of protonated aldose,
and $[S]_T$ = the total aldose concentration

Putting $[SH^+]$ and $[H^+CrO_3]$ in equation *5*, we get

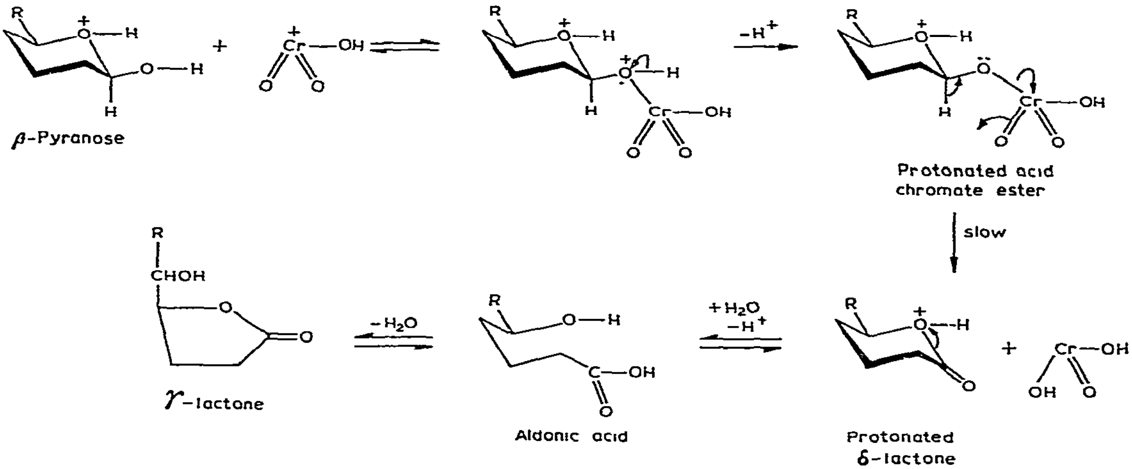
$$V = \frac{k[S]_T\,[HCrO_4^-]\,[H^+]^3}{1 + K_3[H^+]}, \tag{8}$$

where $k = k'K_1K_2K_3$,
or

$$k_{obs} = \frac{k[S][H^+]^3}{1 + K_3[H^+]} \tag{9}$$

Equation *9* thus explains the observed orders obtained in the oxidation of aldopentoses and aldohexoses

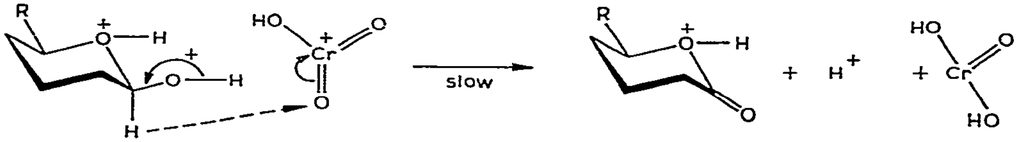
It is well known that aldopentoses and aldohexoses exist mainly as pyranoid and furanoid forms The pyranoid form is generally the most stable, and exists mainly in a chair form The most reactive centre in these compounds is C-1, but the axial or equatorial orientation of HO-1 influences the course and rate of reaction The interaction energies for the chair conformers of the aldohexoses and aldopentoses show[11] that the conformer having HO-1 equatorial is usually the more stable This form undergoes faster oxidation than the corresponding anomer having HO-1 axial This is true for D-galactose, L-arabinose, and D-xylose[11], but for D-mannose, the form having HO-1 axial is preponderant[22], and HO-1 (being less exposed) is less accessible for the oxidant Hence, for D-mannose, the form having HO-1 equatorial may react more rapidly[22] Therefore, it is suggested that the protonated chromic acid reacts with the protonated reactive anomer of the aldoses by a fast step to give an intermediate that then disproportionates slowly to give protonated δ-lactone[11] and chromium(IV) The δ-lactone then undergoes fast and reversible hydrolysis to yield the aldonic acid which, being fairly readily interconvertible into lactones in aqueous solution, also remains in equilibrium with the γ-lactone Chromium(VI) therefore behaves as a 2-equivalent oxidant, since the addition of acrylamide to the reaction mixture failed to give any suspension, indicating that free radicals are not generated in solution The steps of the reaction are shown in Scheme 1 Chromium(IV), which is generated in the rate-determining step, disproportionates[23] or reacts rapidly[24] with chromium(VI) to form chromium(V) The latter finally reacts with the substrate to give the products of oxidation by fast steps, and chromium(V) is reduced to chromium(III)



[R = CH_2OH for aldohexoses, and H for aldopentoses]

Scheme 1

In the present investigation, the intermediate ester (supposed to be formed by the reaction between chromic acid and either aldohexoses or aldopentoses) could not be isolated, and the kinetic evidence[17a] for intermediate ester formation was not significant Again, a linear plot of log k_{obs} against $-H_0$ indicates[25] that a molecule of water cannot form a part of the transition state, and hence is not necessary as catalyst or H^+ abstractor from the ester, the formation of which itself need not be a prerequisite for the oxidation Moreover, the linear relationship between k_{obs} and [Aldose] suggests that the oxidation of aldohexoses and aldopentoses may follow the direct, bimolecular mechanism Thus, alternatively, a bimolecular, electron-switch mechanism, involving hydride transfer from the reactive substrate to the reactive oxidant species, may also take place according to Scheme 2 This is in keeping with the view of Rocek *et al.*[26], which was also conceded by Westheimer and Graham[27] for very strong acid media Since the present investigation was carried out in strong $HClO_4$ (0 8–2 4M), the above mechanism (Scheme 2) may be considered to be plausible



Scheme 2

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