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Kinetic Studies of the Oxidation of Aldopentoses: L-Arabinose and D-Xylose Oxidized by Hexacyanoferrate(III) in an Alkaline Medium

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The kinetic studies of the oxidation of L-arabinose and D-xylose have been carried out using potassium ferricyanide in the presence of sodium hydroxide and sodium carbonate. The order of the reaction has been found to be zero with respect to ferricyanide and first with respect to the reducing sugar. The reaction rate is also directly proportional to the hydroxide ion concentration. The reaction also has a very small induction period.

Kinetic studies of reactions in solutions have achieved commendable importance during the last few decades, especially in explaining the mechanism of the reactions. So far as the kinetics of oxidation of these reducing sugars is concerned, however, this field has not been studied for several years. Most of the works in this direction were first carried out by using halogens[1] as oxidising agents in alkaline and acidic media. Ingels and Israel[2] studied the kinetics of the oxidation of simple monosaccharides as well as of disaccharides by alkaline hypoiodide; they reported the order of the reaction with respect to each reactant to be unity. They also observed that the rates of the oxidation of D-galactose and D-arabinose are greater than those of D-glucose and D-xylose respectively.

Systematic studies of the kinetics of oxidation of several hexoses and pentoses by cupric tartrate and cupric citrate in the presence of sodium hydroxide were made in this laboratory by Singh, Krishna and Ghosh.[3,4] They reported that the reaction is of the first order with respect to the cupric complex and that it is catalysed by the free hydroxide ion. There is also an autocatalysis due to the cuprous oxide produced in the system. Recently Nath and Singh[5,6] studied the kinetics of the oxidation of several aldo and keto hexoses by potassium ferricyanide in an alkaline medium. The advantage of taking potassium ferricyanide as the oxidant lies in the value of its redox potential, which is large compared to that of copper. They have observed that the reaction rate is of the zero order with respect to ferricyanide and of the first order with respect to reducing sugar. Further, the reaction rate is directly proportional to the concentration of hydroxide ions, and the reaction has a small induction period, which is probably due to the presence of oxygen. The present work will deal with the kinetics of the oxidation of L-arabinose and D-xylose by potassium ferricyanide in an alkaline medium; such a study will give more evidence on the mechanism.

Experimental

Potassium ferricyanide was of B. D. H. (AnalaR)-grade sample. The standard solution of reducing sugar was prepared just before starting the reaction. The sugar and the sodium hydroxide used were of E. Merck grade.

The volumetric procedure developed by Lang[7] which depends upon the precipitation of complex zinc-ferrocyanide to complete the reaction between potassium ferricyanide and iodine is not very accurate because it does not give a very clear end point due to the appearance of a bluish colour in the end. Therefore, the present method of estimating ferricyanide was slightly modified by increasing the overall strength of potassium iodide to a great extent instead of by adding zinc sulphate.

The mixture of potassium ferricyanide and alkali was kept in a black-coated jena bottle at a constant temperature (±0.1°C); the fresh solution of reducing sugar was kept separately in the same bath. When the solutions have attained the temperature of the bath, the requisite quantity of reducing sugar was added to a solution containing potassium ferricyanide and alkali. The progress of the reaction was followed by sucking out an aliquot (10 or 5 ml.) and pouring it into a beaker containing 10 ml. of a strong fresh solution of potassium iodide (40%) and 5 ml. of 4 N sulphuric acid of B. D. H. (AnalaR) grade. The function of the sulphuric acid was to check the reaction by neutralising the alkali as well as to help in the liberation of iodine. The liberated iodine was immediately titrated by a standard solution of sodium thiosulphate (hypo), using starch as an indicator and with the help of micro-burette.

Results

The Determination of the Order of Reaction with Respect to Ferricyanide Ions.—In order to find out the order of the reaction with respect to ferricyanide ions, the concentration of the reducing sugar was kept high. If the concentration of the reducing sugar is in a large excess as compared to the concentration of ferricyanide ions, the variation in the velocity of the reaction will mainly be determined by the concentration of the latter. The results given below consistently show that the reaction is of the zero order with respect to ferricyanide ions.

TABLE I

Temp.: 30°C Total vol.: 200 ml.
Aliquot sucked out: 10 ml.
Overall concn.:
$K_3Fe(CN)_6$, 0.0025 M; NaOH, 0.02 N;
L-Arabinose, 0.01 M

Time min.	Vol. of N/420 hypo ml.	$k_0=\frac{\Delta x}{\Delta t}$
0	10.30	—
15	9.45	0.056
30	8.25	0.080
45	7.05	0.080
75	4.90	0.072
90	3.90	0.067
105	2.90	0.067
120	1.75	0.070
∞	0.00	—

Mean k_0 0.072
(Neglecting the first constant)
k_s 1.71×10^{-5}
(mol. l^{-1} min^{-1})

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[1] J. W. Green, *Advan. Carbohydrate Chemistry*, **3**, 129 (1948).

[2] O. G. Ingels and E. C. Israel, *J. Chem. Soc.*, **1948**, 810.

[3] M. P. Singh, B. Krishna and S. Ghosh, "Proceedings of the National Academy of Sciences, India, Section A, Vol. XXVIII, Part I (1959), pp. 21—29; Section A, Vol. XXVIII, Part I, (1959), pp. 39—42.

[4] M. P. Singh, B. Krishna and S. Ghosh, *Z. physik. Chem.*, **204**, 1 (1955); **205**, 285 (1956); **208**, 265 (1958).

[5] N. Nath and M. P. Singh, ibid., **221**, 204 (1962).

[6] N. Nath and M. P. Singh, ibid., **224**, 419 (1963).

[7] R. Lang, *Z. anal. Chem.*, **79**, 161 (1929); **93**, 21 (1937).

TABLE II

Temp.: 40°C Total vol.: 200 ml.
Aliquot sucked out: 10 ml.
Overall concn.:
$K_3Fe(CN)_6$, 0.0025 M; Na_2CO_3, 0.5 N;
L-Arabinose, 0.01 M

Time min.	Vol. of N/374 hypo ml.	$k_0=\frac{\Delta x}{\Delta t}$
0	9.10	—
5	8.25	0.170
10	7.70	0.110
20	6.60	0.110
30	5.50	0.110
40	4.50	0.100
50	3.40	0.110
70	1.25	0.108
∞	0.00	—

Mean k_0 0.110
(Neglecting the first constant)
k_s 2.96×10^{-5}
(mol. l^{-1} min^{-1})

TABLE III

Temp.: 30°C Total vol.: 100 ml.
Aliquot sucked out 5 ml.
Overall concn.:
$K_3Fe(CN)_6$, 0.0025 M; NaOH, 0.01 N;
D-Xylose, 0.01 M

Time min.	Vol. of N/740 hypo ml.	$k_0=\frac{\Delta x}{\Delta t}$
0	9.70	—
10	8.92	0.078
20	7.74	0.118
30	6.54	0.120
40	5.40	0.114
50	4.18	0.122
60	2.92	0.126
70	1.80	0.112
∞	0.00	—

Mean k_0 0.119
(Neglecting the first constant)
k_s 3.21×10^{-5}
(mol. l^{-1} min^{-1})

A perusal of the above tables will show that the zero order velocity constants assume practically constant values after a certain induction period. Below each table the mean value of standard zero order velocity constant (k_s) has been given; each has been calculated by taking the mean zero order velocity constant (k_0) and multiplying it by the factor S/V, where S is the strength of the hypo used in the estimation and V, the volume of the aliquot taken;

$$k_s = k_0\times(S/V)$$

A further confirmation of the order of reaction with respect to ferricyanide can be seen from Tables V and VI.

TABLE IV

Temp.: 35°C Total vol.: 100 ml.
Aliquot sucked out: 5 ml.
Overall concn.:
$K_3Fe(CN)_6$, 0.0025 M; Na_2CO_3, 0.20 N
D-Xylose, 0.01 M

Time min.	Vol. of N/880 hypo ml.	$k_0=\frac{\Delta x}{\Delta t}$
0	11.00	—
10	10.00	0.100
20	8.30	0.170
30	6.80	0.150
40	5.20	0.160
50	3.90	0.130
60	2.40	0.150
70	0.90	0.150
∞	0.00	—

Mean k_0 0.150
(Neglecting the first constant)
k_s 3.408×10^{-5}
(mol. l^{-1} min^{-1})

TABLE V

Temp.: 30°C
Overall concn.:
NaOH, 0.048 N; L-Arabinose, 0.001 M

Concn. of ferricyanide M	Rate const. $k_s\times10^5$ mol. l^{-1} min^{-1}
0.0025	3.5
0.0033	3.7
0.0050	3.7
0.0100	3.7

TABLE VI

Temp.: 30°C
Overall concn.:
NaOH, 0.05 N; D-Xylose 0.001 M

Concn. of ferricyanide M	Rate const. $k_s\times10^5$ mol. l^{-1} min^{-1}
0.0025	15.4
0.0033	15.4
0.0050	15.4
0.0066	15.4

The Effect of Varying the Ferrcyanide Ion Concentration—From Table V, it is evident that though the concentration has been varied from 25×10^{-4} M to 100×10^{-4} M, with the concentrations of other reactants kept the same, the zero order rate constants are practically the same. Table VI confirms the above statement in the case of D-xylose. Thus Tables V and VI also confirm that the reaction is of the zero order with respect to potassium ferricyanide in the concentration range of alkali and potassium ferricyanide studied.

The Determination of the Order of Reaction with Respect to Reducing Sugar. — In order

TABLE VII

Overall concn. of $K_3Fe(CN)_6$: 0.0025 M

	Temp., °C	Overall concn. of NaOH N	Overall concn. of sugar M	Rate const. $k_s \times 10^6$ mol. l^{-1} min^{-1}	$\frac{k_s}{[\text{sugar}]} \times 10^4$
L-Arabinose	30	0.02	0.0200	32.40	16.20
			0.0125	20.10	16.08
			0.0066	11.30	16.95
			0.0050	8.50	17.00
D-Xylose	30	0.02	0.0200	111.6	55.80
			0.0125	75.0	60.00
			0.0066	40.3	60.40
			0.0050	30.5	60.00

TABLE VIII

Overall concn. of $K_3Fe(CN)_6$: 0.0025 M

	Temp., °C	Overall concn. of sugar	Overall concn. of NaOH N	Rate const. $k_s \times 10^6$ mol. l^{-1} min^{-1}	$\frac{k_s}{[\text{NaOH}]} \times 10^4$
L-Arabinose	30	0.01 M	0.0200	17.10	8.55
			0.0125	10.70	8.55
			0.0100	8.33	8.33
			0.0050	4.12	8.24
D-Xylose	30	0.01 M	0.0200	61.00	30.50
			0.0125	39.20	31.36
			0.0100	32.10	32.10
			0.0066	21.00	31.50

to determine the order of reaction with respect to reducing sugar, the concentration of reducing sugar was varied, while the concentration of other reactants was kept constant. It has been shown that the reaction is of the zero order with respect to ferricyanide ions; therefore, the average velocity ($\Delta x/\Delta t$), the instantaneous velocity (dx/dt), and the specific rate constant are identical. If, therefore, the average velocity (the velocity in the case of a zero order reaction) increases in direct proportionality with the increase in the concentration of reducing sugar, it proves that the reaction is of the first order with respect to reducing sugar. The table given below shows the effect of varying the reducing sugar concentration on the zero order velocity constant.

From Table VII it is evident that $k_s/[\text{sugar}]$ gives practically a constant value, which indicates that the reaction rate is directly proportional to the reducing sugar concentration. Thus, it is evident that the order of reaction with respect to reducing sugar is unity.

The Effect of Varying the Hydroxyl Ion Concentration.—A perusal of Table VIII will show that the zero-order velocity constant increases proportionally with the increase in the concentration of hydroxide ions.

Discussion

A careful study of the kinetics of the oxidation of the above sugars shows that the rate of expression is of the form:

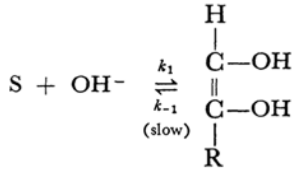
$$-\frac{d[\text{Fe(CN)}_6{}^{3-}]}{dt} = k[\text{sugar}][\text{OH}^-]$$

which implies that the rate of reaction is independent of the concentration of ferricyanide ions, while the reaction is of the first order both with respect to reducing sugar as well as to alkali. In cases where the concentration of the sugar as well as of alkali is large as compared to the concentration of ferricyanide, the rate expression takes the form:

$$-\frac{d[\text{Fe(CN)}_6{}^{3-}]}{dt} = k_s = \frac{\Delta \chi}{\Delta t}$$

where $k_s = k[\text{sugar}][\text{OH}^-]$

Further, on the basis of the above experimental results, it appears that the first slow step involves a reaction between hydroxide ions and the reducing sugar, leading to the formation of an intermediate reactive form:



$$S + OH^- \underset{\substack{k_{-1} \\ (\text{slow})}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c} H \\ | \\ C{-}OH \\ \| \\ C{-}OH \\ | \\ R \end{array} \qquad (\text{1st step})$$

(1, 2 enediol)

where S represents the reduing sugar. The fact that this step is slow explains how the order of the reaction is unity with respect to reducing sugar. Further, this intermediate reactive form, which is called "1, 2 enediol," is subsequently oxidised by ferricyanide to give ferrocyanide and other reaction products:

$$\text{en} + [\text{Fe(CN)}_6{}^{3-}] \xrightarrow[\text{fast}]{k_2} [\text{Fe(CN)}_6{}^{4-}] + \text{other reaction product} \qquad \text{(2nd step)}$$

where "en" represents "1, 2 enediol." The fact that the second step is fast explains the zero order of the reaction with respect to ferricyanide ions. Further work on the kinetics of the oxidation of several more reducing sugars is now in progress; the details will be published later.