which catalyze cyclodimerization[16] are of the first transition series and hence favor lower coordination numbers.

Experimental Section

All experiments were carried out under an atmosphere of prepurified nitrogen in previously dried equipment. Reactions were conducted in either a conventional three-necked flask or 7-oz clear-glass beverage bottles sealed with perforated metal caps with a neoprene rubber liner.

Gas–liquid partition chromatography (glpc) analyses were performed on an F & M Model 720 or a Hewlett-Packard Model 5750 chromatograph, using a 10 ft × 0.25 in. copper tube column packed with 20% DC 200 silicone fluid on 35–80 mesh Chromosorb P. The chromatographs were run isothermally at *ca.* 100° with helium carrier gas flow rate of 100–200 ml/min. Areas were determined using a disk integrator.

The molybdenum complex, $(C_5H_5N)_2Mo(NO)_2Cl_2$, was prepared by the procedure of Cotton and Johnson.[17] The aluminum alkyls were purchased from Texas Alkyls and used without further purification. In catalyst preparation the aluminum alkyls were used as 1 *M* solutions in chlorobenzene. The chlorobenzene was Fisher or Mallinckrodt distilled from calcium hydride and stored over molecular sieves under nitrogen. The 2-pentene was Phillips pure grade and was purified by passage through a column of activated silica and magnesium oxide. The 4-nonene (n^{20}D 1.4162) was from Aldrich Chemical Co. and used as received.

The following general procedure was used in all kinetic experiments. The molybdenum complex and chlorobenzene were placed in the reaction vessel. The solution of aluminum alkyl in chlorobenzene was injected into the mixture. The catalyst-formation reaction was generally allowed to proceed for 1–1.5 hr at room temperature with magnetic stirring. The reaction vessel then was placed in an insulated ice bath. After *ca.* 15 min the olefin was injected into the catalyst solution. Samples of the reaction mixture were taken *via* a 1-cc hypodermic syringe through a rubber septum on the side arm of the flask or through the rubber stopper of the bottle. The samples were immediately injected into a capped Diels–Alder tube containing water to terminate the reaction. In the experiments dealing with determination of the activation energies, the temperature was maintained to within ±0.5°.

Acknowledgment. I am indebted to Drs. D. L. Crain and E. A. Zuech for helpful general discussion and to Dr. A. J. Moffat for discussions concerning the kinetic data.

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Mechanism of Copper(II) Oxidation of Reducing Sugars. I. Kinetics and Mechanism of Oxidation of D-Xylose, L-Arabinose, D-Glucose, D-Fructose, D-Mannose, D-Galactose, L-Sorbose, Lactose, Maltose, Cellobiose, and Melibiose by Copper(II) in Alkaline Medium

S. V. Singh,[1] O. C. Saxena, and M. P. Singh

Contribution from the Department of Chemistry, University of Allahabad, Allahabad 2, India.
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Abstract: Kinetic studies of Cu^{II} oxidation of two pentoses, five hexoses, and four disaccharides have been carried out in alkaline medium. The reaction showed a first-order dependence with reducing sugar and alkali concentration, and the oxidation process is independent of Cu^{II} concentration in the case of all the reducing sugars. A single rate expression, $-d[Cu^{II}]/dt = k[S][OH^-]$, and one scheme of mechanism have been proposed. It is found that the rate of oxidation is the rate of enolization in the case of all the reducing sugars.

Kinetics of Cu^{II} oxidation of reducing sugars was first studied by Urech[2a] to elucidate the structure of the milk of sugar, in which, of course, he succeeded but did not put forward any detailed mechanism of the oxidation process. Thereafter, Singh, Krishna, and Ghosh[2b] studied the kinetics of oxidation of some hexoses and pentoses by alkaline cupric tartrate and citrate. They found that the rate of reaction is first order with respect to the reducing sugar and independent of Cu^{II} concentration, irrespective of the amount of complexing agents, and explained that observed rates of oxidation of reducing sugars correspond to their rates of enolization. Later, Marshall and Waters,[3] in their kinetic study of the oxidation of D-glucose, acetoin, and benzoin by alkaline Cu^{II} complexed with tartrate, citrate, and picolinate, etc., confirmed the result of Singh, *et al.*, and reported that the rates of enolization of acetoin and benzoin are greater than their rates of oxidation. They gave the rate expression as $-d[Cu^{II}]/dt = 2K_4[E]\cdot[Cu^I]$, and showed that cuprous chelate formation is the rate-determining step. Recently Wiberg and Nigh[4] have studied the oxidation of hydroxyacetophenone by Cu^{II} in buffered aqueous pyridine base in order to verify the ingenious explanation postulated by Marshall and Waters[3] and observed that the rate law is $v = K_1\cdot[\text{ketol}] + K_2[\text{ketol}][Cu^{II}]$. The first term of the right-hand side corresponds to the independently determined

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[1] Address all communications to this author at the Department of Chemistry, Birla Institute of Technology, Mesra, Ranchi, Bihar, India.

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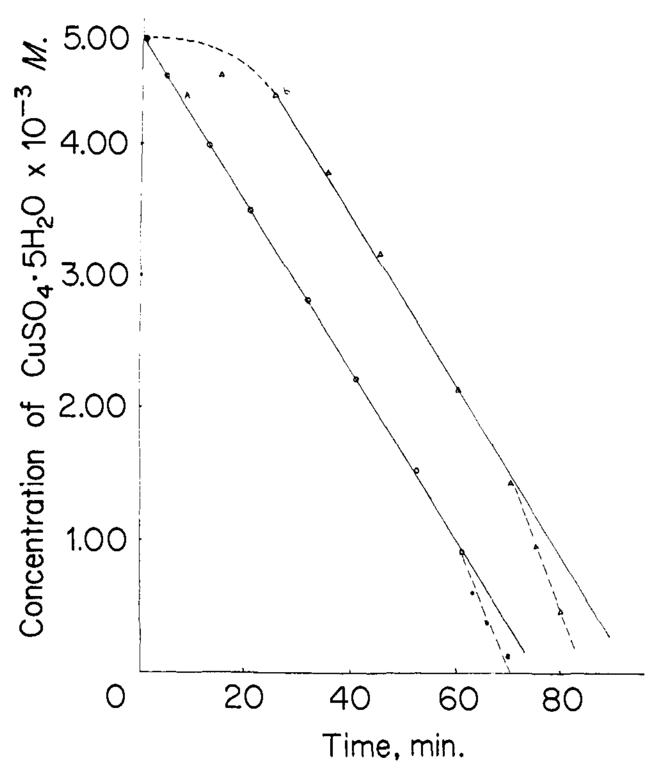

Figure 1. Temperature 35°; [lactose] 1.00 × 10^{-2} *M*; [NaOH] 5.00 × 10^{-2} *N*; A, with nitrogen; B, without nitrogen; k_5 = 6.54 × 10^{-5} mole l.$^{-1}$ m^{-1}.

rate of enolization and the second term is the major one when Cu^{II} concentration is greater than 0.01 *M*. Thus at lower concentrations of Cu^{II} they support the explanation of Singh, *et al.*,[2] and do not agree with the view of Marshall and Waters.[3]

In order to postulate a complete, concise, and general mechanism of Cu^{II} oxidation of reducing sugars in alkaline medium and to verify the results of previous workers, we have conducted the present study which deals with the kinetic investigations of oxidation of D-xylose, L-arabinose,[5] D-glucose, D-fructose, D-mannose, D-galactose, L-sorbose, lactose, maltose, cellobiose, and melibiose.

Results and Discussion

Before dealing with actual experimental results it is necessary to point out that in the present study no complexing agents (tartrate, citrate, picolinate, etc.) were used as applied by previous workers, because reducing sugars themselves formed soluble complex with cupric ion within the experimental range of concentrations of reactants. This complex has a blue color similar to Benedicts and Fehlings solution. Attempts were made to study the complex formation between cupric ion and reducing sugar but no reliable data could be obtained because the reaction started only a few minutes after mixing the reagents.

The initiation of the reaction was carried out by mixing 50 ml of sodium hydroxide and 50 ml of cupric sulfate and reducing sugar, both kept in separate black-coated jena flasks immersed in an electrically regulated thermostat. The rate of oxidation was followed by estimating the remaining Cu^{II} iodometrically.

Within the range of concentrations studied of reducing sugar, cupric sulfate, and sodium hydroxide, no precipitate of cupric hydroxide was produced by mixing basic solution and cupric ion solution and the reaction mixture was perfectly homogeneous before the reaction started. However, it did not remain homogeneous throughout because of the formation of cuprous oxide as a heterogeneous reaction product during kinetic runs.

The oxidation of these reducing sugars by Cu^{II} in the presence of sodium hydroxide started after a slight induction period but became independent of oxidant concentration with a brief autocatalysis in the latter part of the reaction.

The first feature, the induction period, is entirely eliminated by removal of dissolved oxygen before the reaction is initiated, *i.e.*, when the experiments were carried out in nitrogen atmosphere (Figure 1). The other feature, the autocatalysis, is due to the catalytic role of cuprous oxide produced as a heterogeneous reaction product during kinetic runs. The effect of this autocatalysis is the increase of zero-order velocity constant k_0 during the course of reaction. When the reaction is slow k_0 is uniform and autocatalysis is observed only in the latter part of the reaction. Autocatalysis is more prominent at higher concentrations of the reactants and temperature. In such cases the cuprous oxide produced is in finer colloidal particles and the autocatalysis is observed during the entire course of reaction. Tables I and II illustrate the above findings.

Table I[a]

Time, min	(15.87 × 10^{-4} *N*) Hypo, ml	$k_0 \times 10^2$	Time, min	(14.28 × 10^{-4} *N*) Hypo, ml	$k_0 \times 10^2$
0	7.90		0	8.76	
17	7.88	0.11	20	8.00	3.80
20	7.62	8.66	30	7.30	7.00
30	6.76	8.60	40	6.62	6.80
45	5.50	8.40	50	5.92	7.00
55	4.54	9.60	60	5.22	7.00
68	3.20	10.30	70	4.52	7.00
75	1.84	19.00	80	3.80	7.20
∞	0.00		90	3.10	7.00
			100	2.32	7.80
			110	1.30	10.20
			∞	0.00	

[a] Temperature 35°; ($CuSO_4 \cdot 5H_2O$) 2.50 × 10^{-3} *M*, ($CuSO_4 \cdot 5H_2O$) 2.5 × 10^{-3} *M*, (NaOH) 5.00 × 10^{-2} *N*, (NaOH) 2.0 × 10^{-2} *N*, (lactose) 5.00 × 10^{-3} *M*, (lactose) 6.66 × 10^{-3} *M*.

The rate law and mechanism have been derived by studying the effect of varying concentrations of the reactants on rate constants. Tables III, IV, and V show the effect of variation of concentrations of Cu^{II}, reducing sugars, and sodium hydroxide, respectively.

The fact that the stoichiometry was found to involve 6 moles of Cu^{II} for each mole of reducing sugar consumed makes it adequately certain that the rate of the reaction is determined by the decrease in the concentration of Cu^{II}. Standard zero-order velocity constants have been calculated by multiplying k_0 by *X*/*V*; *X* is the strength of the titrant *V* is the volume of aliquot taken, and k_0 is the usual zero-order velocity constant ($k_0 = \Delta c/dt$). Table III shows the decrease in values of k_s with increasing concentration of Cu^{II}. When Cu^{II}

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Table II[a]

Time, min	(22.16 × 10^{-4} *N*) Hypo, ml	$k_0 \times 10^2$	Time, min	(22.16 × 10^{-4} *N*) Hypo, ml	$k_0 \times 10^2$
0	4.52		0	9.24	
5	4.52		10	9.24	
10	4.44	1.60	20	9.20	0.40
15	4.10	6.80	30	9.00	2.00
20	3.76	6.80	40	8.46	5.40
25	3.40	7.20	60	7.38	5.40
30	3.00	8.00	80	6.22	5.80
40	2.00	10.00	100	5.14	5.40
50	0.66	13.40	120	4.00	5.70
∞	0.00		140	2.46	7.70
			∞	0.00	

[a] Temperature 35°; [$CuSO_4 \cdot 5H_2O$] 2.00 × 10^{-3} *M*, [$CuSO_4 \cdot 5H_2O$] 2.50 × 10^{-3} *M*, [NaOH] 2.00 × 10^{-2} *N*, [NaOH] 2.00 × 10^{-2} *N*, [maltose] 1.00 × 10^{-2} *M*.

Table III. Effect of Cu^{II} Concentration on the Rate of Oxidation

Temp, °C	Concn of reducing sugar and alkali × 10^2 *M*	[Cu^{II}] × 10^4 *M*	[Free OH^-] × 10^3 *M*	$k_s \times 10^5$ mole $l.^{-1}$ min^{-1}	k_s/[free OH^-] × 10^4
30	D-Xylose 1.0	20.0	96.0	3.37	3.51
	NaOH 10.0	25.0	95.0	3.55	3.74
		35.0	93.0	3.50	3.63
35	L-Arabinose 1.0	20.0	496.0	6.66	1.34
	NaOH 50.0	30.0	494.0	6.11	1.22
		40.0	492.0	6.00	1.22
45	D-Mannose 1.0	25.00	95.00	4.00	4.21
	NaOH 10.0	28.00	94.00	3.65	3.86
		50.00	90.00	3.30	3.66
35	D-Galactose 1.0	25.00	28.00	6.44	23.00
	NaOH 3.3	33.00	26.50	5.52	20.68
		50.00	23.00	4.50	19.56
		60.00	19.80	3.68	18.58
35	D-Glucose 2.00	25.00	45.00	12.60	28.00
	NaOH 5.00	28.00	44.40	12.10	27.25
		30.00	43.40	11.60	26.73
		50.00	40.00	11.30	28.35
		100.00	30.00	7.90	26.33
30	D-Fructose 1.00	25.00	15.00	6.45	43.00
	NaOH 2.00	30.00	13.00	5.65	43.44
		40.00	12.00	5.00	41.66
		50.00	10.00	3.95	39.50
30	L-Sorbose 1.00	25.00	15.00	8.00	53.33
	NaOH 2.00	33.00	13.40	6.40	47.96
		40.00	12.00	6.50	54.10
		50.00	10.00	5.54	55.40
35	Lactose 1.00	25.00	45.00	7.64	17.0
	NaOH 5.00	33.33	43.33	6.41	14.8
		40.00	42.00	6.82	15.4
		50.00	40.00	6.51	16.3
		100.00	30.00	4.62	15.4
35	Maltose 1.00	20.00	16.00	3.01	18.8
	NaOH 2.00	25.00	15.00	2.83	18.8
		33.33	13.40	2.80	21.6
		40.00	12.00	2.45	20.4
		50.00	10.00	2.21	22.1
35	Melibiose 1.00	20.00	16.00	4.11	25.7
	NaOH 2.00	25.00	15.00	3.73	24.8
		30.00	14.00	3.48	24.8
		40.00	12.00	3.40	28.3
35	Cellobiose 1.00	20.00	6.00	3.68	61.3
	NaOH 1.00	25.00	5.00	3.42	68.4
		30.00	4.00	2.73	68.2

Table IV. Effect of Reducing Sugar Concentration Variation on the Rate of Oxidation

Temp, °C	Concn of NaOH × 10 *M*	Concn of Cu^{II} × 10^3 *M*	Concn of sugar × 10^3 *M*	$k_s \times 10^5$ mole $l.^{-1}$ min^{-1}	k_s/[sugar] × 10^4
25	1.00	2.50	D-Xylose		
			20.00	4.80	24.00
			12.50	2.74	21.80
			10.00	1.60	16.50
30	5.00	2.50	L-Arabinose		
			12.50	4.40	35.2
			10.00	3.33	33.3
			7.14	2.84	39.7
35	0.50	10.0	D-Glucose		
			40.00	14.4	3.6
			20.00	7.0	3.5
			10.00	3.7	3.7
25	0.25	5.00	D-Fructose		
			40.00	6.00	15.00
			20.00	3.00	15.00
			10.00	1.42	14.20
25	0.25	5.00	L-Sorbose		
			40.00	10.00	25.00
			20.00	5.10	25.50
30	1.00	5.00	D-Galactose		
			40.00	28.00	27.00
			20.00	12.00	60.00
45	1.00	5.00	D-Mannose		
			20.00	6.50	3.25
			10.00	3.30	3.30
35	0.10	2.50	Cellobiose		
			20.00	8.08	4.04
			12.50	3.42	2.73
			10.00	3.35	3.35
			5.00	1.79	3.58
35	0.20	2.50	Melibiose		
			20.00	10.11	5.05
			12.50	5.07	4.05
			10.00	3.73	3.73
			5.00	2.01	4.02
35	0.20	2.50	Maltose		
			25.00	7.08	2.83
			20.00	6.00	3.00
			12.50	3.52	2.81
			10.00	1.46	2.83
35	0.50	2.50	Lactose		
			20.00	16.11	8.05
			10.00	7.65	7.65
			6.66	5.80	8.71
			5.00	2.79	5.58

concentration increases there is a decrease in the concentration of hydroxyl ions, because Cu^{II} liberates two protons while forming a complex with reducing sugar. As such when the values of k_s are divided by the corresponding free hydroxyl ion concentration a fairly constant value is obtained in the case of each reducing sugar. This indicates the independency of the reaction rate with the concentration of oxidant. The concentration of free hydroxyl ions is obtained by subtracting twice the concentration of cupric sulfate from that of sodium hydroxide initially taken. Further, when the moles of Cu^{II} concentration are plotted against time a straight line is obtained, confirming the independency of the reaction rate with Cu^{II} (Figure 1).

Table IV shows that the values of k_s, in the case of each reducing sugar, increase in direct proportion with the increase in concentration of reducing sugar and, as such, when divided by the corresponding reducing sugar concentration a fairly constant value is obtained. In other words the reaction is first order with respect to the reducing sugar. Table VI confirms the above finding.

Table V indicates that on dividing the values of k_s by free hydroxyl ion concentration practically constant

Table V. Effect of Variation of NaOH on the Rate of Oxidation

Temp, °C	[NaOH] × 10² *M*	[Free OH⁻] × 10² *M*	[Cu^{II}] × 10³ *M*	[Sugar] × 10² *M*	k_s × 10⁵ mole l.⁻¹ min⁻¹	k_s/[free OH⁻] × 10⁴
25	40.00	39.5	2.50	D-Xylose		
	20.00	19.5		1.00	5.36	1.34
	10.00	9.5			3.41	1.23
					1.40	1.57
35	100.00	99.5	2.50	L-Arabinose	8.40	0.844
	50.00	49.5		1.00	5.33	1.076
35	33.3	32.8	2.50	D-Mannose	3.00	0.91
	20.0	19.5		1.00	2.00	1.02
	12.5	12.0			1.35	1.12
	10.0	9.5			1.00	1.05
30	10.0	9.0	5.00	D-Galactose	7.00	7.70
	5.0	4.0		1.00	3.10	7.70
	3.3	2.3			1.85	8.00
	2.5	1.5			1.12	7.40
25	5.0	4.0	5.00	L-Sorbose	9.33	23.33
	3.3	2.3		1.00	5.14	21.90
	2.5	1.5			4.31	28.70
25	2.5	1.5	5.00	D-Fructose	2.16	14.40
	2.0	1.00		1.00	1.50	15.00
	1.66	0.66			1.00	15.10
25	20.0	19.00	5.00	D-Glucose	4.40	2.30
	10.0	9.00		1.00	1.97	2.10
	2.5	1.50			0.38	2.50
35	5.0	4.5	2.5	Lactose	7.64	17.00
	4.0	3.5		1.00	6.01	17.10
	2.5	2.0			5.00	25.00
	2.0	1.5			2.56	17.10
	1.25	0.75			1.04	14.00
35	5.0	4.50	2.5	Maltose	8.06	13.00
	4.0	3.50		1.00	6.37	13.20
	3.333	2.833			5.16	13.50
	2.50	2.00			3.92	19.60
35	5.00	4.50	2.5	Melibiose	10.10	22.40
	4.00	3.50		1.00	8.03	22.90
	2.00	1.50			3.73	24.80
	1.25	0.75			2.10	28.00
35	2.50	2.00	2.5	Cellobiose	10.75	53.70
	2.00	1.50		1.00	9.70	64.60
	1.25	0.75			4.13	55.10
	1.00	0.50			3.35	67.01

Table VI[a]

Time, min	(15.38 × 10⁻³ *M*) Ce(SO₄)₂, ml	k_1[b] × 10³ min⁻¹
0	0.00	
10	0.70	9.67
20	1.34	9.69
30	1.80	9.86
60	3.28	9.41
90	4.04	9.41
135	5.50	9.53
190	6.28	9.21
270	6.52	9.23
∞	7.60	

[a] Temperature 40°; [lactose] 2.00 × 10⁻³ *M*, [NaOH] 5.78 × 10⁻¹ *N*, [$CuSO_4 \cdot 5H_2O$] 1.00 × 10⁻¹ *M* (complexing agent glycerol 10 ml). [b] k_1 is the first-order rate constant.

values are obtained. This leads to the conclusion that the reaction rates are also directly proportional to the free hydroxyl ion concentration, which is evident further from the fact that a plot of k_s against free OH⁻ concentration is a straight line (Figure 2).

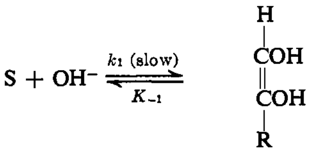
The above data indicate that the rate law is

$$\frac{d[\mathrm{Cu^{II}}]}{dt} = k[\mathrm{S}][\mathrm{OH^-}] \qquad (1)$$

when Cu^{II} concentration is not greater than 0.01 *M*.

In the above equation S stands for reducing sugar and *k* for specific rate constant.

Since in the presence of alkali reducing sugars undergo tautomeric change through an intermediate enediol, it appears that the rate-determining step in the oxidation process is the action of alkali on reducing sugar leading to a slow transformation, giving 1,2-enediol.



$$\mathrm{S + OH^-} \underset{K_{-1}}{\overset{k_1\ (\text{slow})}{\rightleftharpoons}} \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{COH}\\ \|\\ \mathrm{COH}\\ |\\ \mathrm{R}\end{array} \qquad \text{(I)}$$

E, 1,2-enediol

$$\mathrm{E + Cu^{II}} \xrightarrow{k_2\ (\text{fast})} \underset{\mathrm{P}}{\text{enediol–Cu}^{\mathrm{II}}\ \text{intermediate complex}} \xrightarrow{k_3\ (\text{fast})} \mathrm{Cu_2O} + \text{other reaction products} \qquad \text{(II)}$$

$$\mathrm{P + O_2} \longrightarrow \mathrm{Cu^{II}} + \text{other reaction products} \qquad \text{(III)}$$

Steps II and III explain the independency of the reaction rate with Cu^{II} and induction period, respectively. Now

$$\frac{d[\mathrm{E}]}{dt} = k_1[\mathrm{S}][\mathrm{OH^-}] - k_{-1}[\mathrm{E}] - k_2[\mathrm{E}][\mathrm{Cu^{II}}] \qquad (2)$$

At stationary state $d[E]/dt = 0$; therefore

$$[E] = \frac{k_1[S][OH^-]}{k_{-1} + k_2[Cu^{II}]} \qquad (3)$$

From step II

$$-\frac{d[Cu^{II}]}{dt} = k_2[E][Cu^{II}] \qquad (4)$$

Substituting for [E]

$$\frac{-d[Cu^{II}]}{dt} = \frac{k_2k_1[S][OH^-][Cu^{II}]}{k_{-1} + k_2[Cu^{II}]} \qquad (5)$$

$$\frac{-d[Cu^{II}]}{dt} = \frac{k_1[S][OH^-][Cu^{II}]}{\frac{k_{-1}}{k_2} + [Cu^{II}]} \qquad (6)$$

Step II is very fast ($k_2 \gg k_{-1}$), hence k_2/k_{-1} can be neglected. Thus eq 6 assumes the form

$$\frac{-d[Cu^{II}]}{dt} = k_1[S][OH^-] \qquad (7)$$

where k_1 is identical with k of eq 1.

Equation 7 clearly represents the rate equation of the oxidation of reducing sugars by Cu^{II} in alkaline medium and completely justifies the experimental results, *i.e.*, the rate of oxidation is directly proportional to the concentration of reducing sugar and free hydroxyl ions and independent of concentration of the oxidant Cu^{II}.

Evidence of an enediol from the sugars in alkaline solution is afforded by the ability of alkaline sugar solutions to take up large quantities of iodine,[6] by observation that sugars are oxidized with cleavage between C_1 and C_2 in alkaline solutions,[7] and by the studies of the ultraviolet absorption spectra[8] (which show a maximum characteristic of dicarbonyl compounds attributed to an enediol). Further evidence for the formation of an enediol is furnished by the observed ability of alkaline solutions of carbohydrates to decolorize the solution of 2,6-dichlorophenolindophenol.[9]

In the case of oxidation of reducing sugars by cupric tartrate and citrate complexes Wiberg and Nigh[4] gave their explanation that in the presence of tartrate and citrate complex formation between Cu^{II} and reducing sugar is not possible and so the reaction is zero order with respect to Cu^{II} concentration. However, this assumption is not in agreement with our experimental results, because from our data it is evident that the reaction with respect to Cu^{II} is zero order even in the absence of complexing agents (tartrate, citrate, etc.).

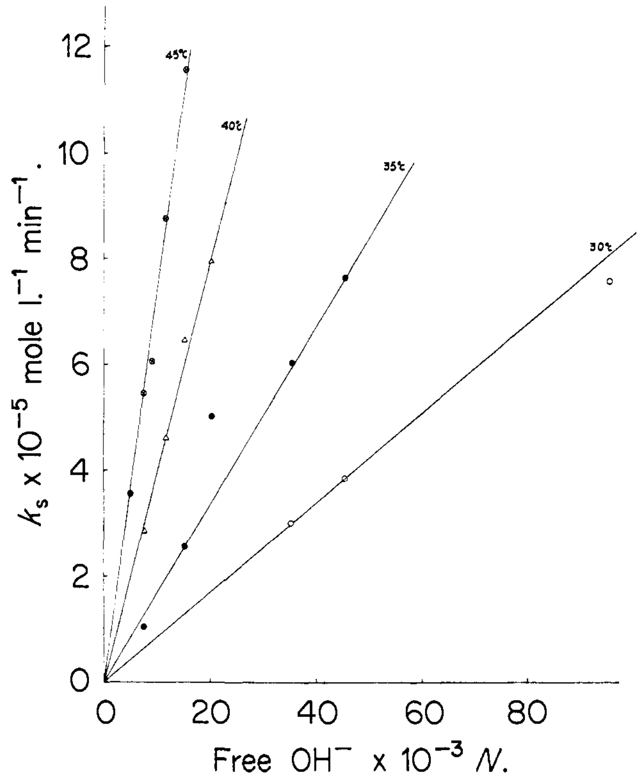


Figure 2. [$CuSO_4 \cdot 5H_2O$] 2.50×10^{-3} *M*; [lactose] 1.00×10^{-2} *M*

We can now say that the rate expression obtained from the proposed mechanism of oxidation of reducing sugars indicates that the rate of enolization is their rate of oxidation. A support to the above proposed mechanism has further been afforded by the present authors after studying the kinetics of interconversion of D-glucose and D-fructose in the presence of 1 *N* NaOH and buffer of sodium carbonate and bicarbonate (pH 10.2) which is dealt with in Part II.

In the case of oxidation of reducing sugars by alkaline ferricyanide also, Singh and Nath[10] have shown that the rate of enolization is the rate of oxidation.

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