

KINETICS AND MECHANISM OF MnO_4^- INDUCED REDUCTION OF Hg (II) CHLORIDE BY FRUCTOSE

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ABSTRACT

Oxidation of fructose by neutral permanganate yields a variety of products. Fructose undergoes both terminal group oxidation and C–C cleavage. It can be concluded from fractional order dependence that the reaction has a chain mechanism. The permanganate ion in neutral medium is capable of bringing about oxidation by a simple one electron abstraction process. The results are accounted for by a sequence of free radical reactions.

Key words : Kinetics, Permanganate, Reduction, Fructose, Mercuric chloride.

INTRODUCTION

Various products are reported^{1–6} in the oxidation of fructose by various oxidants. Nevertheless, the nature of the oxidant employed also affects the resulting products. No information on the reduction of Hg (II) chloride by fructose, employing permanganate as the inducing ion, has previously been reported. The aim, herein, is to ascertain the oxidative degradation products of fructose by MnO_4^- ion and the elucidation of their role in reducing Hg (II) chloride to Hg (I) state. The possible mechanistic steps are discussed.

EXPERIMENTAL

All chemicals used were of B.D.H. (Analar) or Merck (C.P.) grade. The kinetics of Hg (II) chloride reduction under different conditions were followed by estimating precipitating calomel at different time intervals by a volumetric estimation. Products of oxidation were separated by T.L.C. and identified by standard spot tests⁷.

RESULTS AND DISCUSSION

Preliminary experiments showed that this induced reduction reaction is attended by an initial period of induction and it takes a long time to acquire a measurable rate. The length of the induction period is observed to depend upon temperature and reactant concentrations. (Table 1 and 2).

Table 1. Variation of Induction Period with Temperature

[HgCl ₂] = 0.02 M		[Fructose] = 0.5 M		[KMnO ₄] = 0.02 N	
Temperature in °C	60	70	99.5		
Induction period (min)	10	5	3		

Table 2. Variation of Induction period with Initial Fructose

[HgCl ₂] = 0.02 M		[KMnO ₄] = 0.02 N		Temp. = 60°C	
Fructose	0.02 M	0.04 M	0.05 M	0.5 M	1.0 M
Induction period in time (min)	130	100	90	10	4

A typical set of kinetics is recorded in Table 3 showing rate variation with time. It can be noted that the reduction commences after an initial period of induction (i.e., 10 mins.) to about 33.0% in a period of six hours, which is fast initially for a short interval of 15 minutes, whereafter a steady rate drop is obtained.

Table 3.

[HgCl ₂] = 0.02 M		[Fructose] = 0.5 M		[KMnO ₄] = 0.02 N	
Induction Period = 10 min.				Temp. = 60°C	
Time (min)	KIO ₃ (mL) x	C = (a-x) KIO ₃ (mL)	[Hg(I)Cl ₂] x 10 ³ moles L ⁻¹	10 ⁵ x k (moles L ⁻¹ min ⁻¹)	
0.0	0.00	20.00	0.000	—	
15.0	1.60	18.40	0.800	5.33	
30.0	2.40	17.60	1.200	4.00	
60.0	3.25	16.75	1.625	2.71	
120.0	4.40	15.60	2.200	1.83	
180.0	5.20	14.80	2.600	1.44	
240.0	5.80	14.20	2.900	1.21	
300.0	6.30	13.70	3.150	1.05	
360.0	6.60	13.40	3.300	0.92	

Similar kinetics was performed with same concentrations at different temperatures. It may be inferred that the overall reaction velocity increases with the rise in temperature. Variation of the reduction rate with initial concentration of the reactants was evaluated over a ten fold concentration range (Table 4).

Table 4. Initial Rate as a Function of Initial Concentration of Reactants

[Hg Cl ₂] = 0.02 M [KMnO ₄] = 0.02 N			[Fructose] = 0.5 M [KMnO ₄] = 0.02 N			[HgCl ₂] = 0.02 M [Fructose] = 0.5 M		
a			b			c		
[Fructose]	10 ⁵ AV. k	10 ⁵ k [Fr.] ^{0.4}	[HgCl ₂] M	10 ⁵ R	10 ⁵ k [Hg Cl ₂] ^{0.3}	KMnO ₄ N	10 ⁵ k	10 ⁵ k [KMnO ₄] ^{0.6}
0.04	0.829	3.0	0.005	1.774	8.7	0.005	1.19	2.8
0.05	0.901	3.0	0.010	2.500	9.5	0.01	1.83	2.9
0.10	1.246	3.1	0.020	2.708	8.7	0.02	2.70	2.8
0.50	2.311	3.0	0.040	3.382	8.9	0.04	4.05	2.8
1.00	3.119	3.1	0.050	3.548	8.7	0.05	4.65	2.8

The data of Table 4 reveal the rate law to have the form :

$$d[\text{Hg}^+]/dt = K [\text{Fr.}]^{0.4} [\text{Hg Cl}_2]^{0.3} [\text{KMnO}_4]^{0.6}$$

Product Analysis

Isolation, identification and estimation of the reaction products were carried out. Table-5 enlists the constituents of the volatile and non-volatile fractions.

Table 5.

Volatile	Non-volatile	Gaseous
Formaldehyde	D-arabinoic, Carbon dioxide	
Formic acid	glycolic and oxalic acid; MnO ₂	

It may be inferred that fructose on oxidation by neutral permanganate yields a variety of products, which lead one to conclude that C₅, C₂ and C₁ compounds are produced in the ketose oxidation. Evidently, fructose undergoes both terminal group oxidation and C-C cleavage.

From fractional order dependences, it is inferred that the reaction has a chain mechanism. The probable steps of which could be as follows:

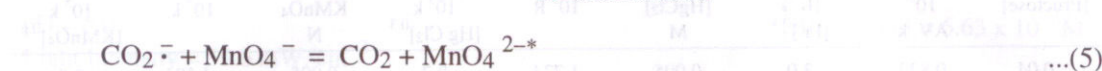
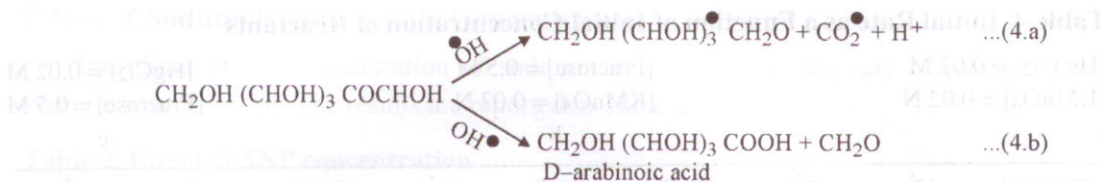
MECHANISM

Chain Initiation Sequence



Chain Propagation Sequence





Manganate soon disproportionates into MnO_2 and this has actually been observed in the reaction. Acceleration due to the precipitated MnO_2 is not evidenced.



Chain Termination Sequences

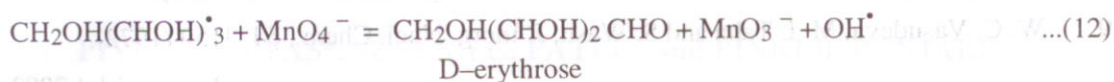
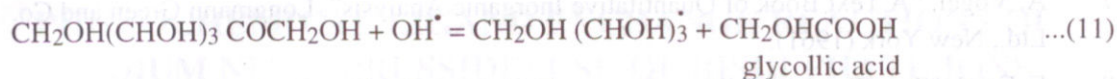


To interpret mechanistically the reduction of $\text{Hg}(\text{II})$ chloride by the oxidation products of fructose (by the MnO_4^- ion), the chain initiation is ascribed to the reaction (1).

The permanganate ion in neutral medium is capable of bringing about oxidation by a simple one electron abstraction process, where reaction takes place between a water molecule and a permanganate ion producing the hydroxyl radicals, which are the active oxidising entities. Ketohexose then undergoes degradation to $\text{CO}_2\cdot$ free radical. The reduction of $\text{Hg}(\text{II})$ is attributed to this free radical.

The $\text{OH}\cdot$ radicals undergo further reactions with fructose (sequence 2 and 4) to give free radicals, which could react, with permanganate and $\text{Hg}(\text{II})$ (sequence 5). Reaction with the former (sequence 5) accounts for the increased rate of its disproportionation to $\text{Mn}(\text{IV})$ in the presence of additive (fructose), while reaction with the latter results in calomel precipitation (sequence 6).

It is believed that the oxidation of fructose by the permanganate ion takes place by two concurrent pathways. Formation of formaldehyde indicates the oxidative fission of the $\text{C}_1\text{--C}_2$ bond by $\text{OH}\cdot$ radicals. The remaining 5 carbon atom compound could be D-arabinoic acid in this case. The tentative mechanism of which is represented in equation (4b). On the other hand, the identification of glycollic acid, as one of the oxidation products, suggests the oxidative cleavage of $\text{C}_2\text{--C}_3$ bond. Under such circumstances, erythrose could be 4 carbon atom compound produced. The tentative mechanism of which as follows :



In the presence of a limited supply of the oxidant, an aldehyde can be a terminating step as revealed by the work of Vasudeva *et al.*⁸ Thus, the aldotetrose formed in reaction (12) could be chain terminating.

Thus, reaction (12) could be a terminating step such as the reaction (4b) while reaction (4a) and (11) are the chain propagation sequences of the induced reduction reaction mechanism.

In consistency with this proposed mechanism, we report that,

1. Permanganate disproportionates at a much faster rate as a result of the reactions (1), (3) and (5).
2. The pH of the system remains steady with time due to the sequence reactions (1), (4), (8), (9) and (10).
3. Evolution of CO₂, identification of glycollic acid and formaldehyde (indicative of the degradation of the carbohydrate molecule) support the above steps.
4. The period of induction is the initial lapse of time for the reducing radical to be formed. Increase of temperature and reactant concentrations correspondingly decrease this period by contributing to reaction (4).

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