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Hg(II) Chloride Reduction to Hg(I) Chloride by MnO_4^- Oxidised D-fructose Products

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Fructose on oxidation with neutral permanganate yields a number of products which leads one to conclude that C_5, C_2 and C_1 compounds are produced. Fructose undergoes both terminal group oxidation and C–C cleavage. Formation of formaldehyde indicates the oxidation fission of the C_1–C_2 bond by $OH^{\cdot}$ radical.

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 work seems to have been done on the kinetics of the oxidation of fructose with neutral permanganate. 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 calomel. The possible mechanistic steps are discussed.

EXPERIMENTAL

All chemicals used were either of B.D.H. (AnalaR) or Merck (C.P.) grade. The kinetics of Hg(II) chloride reduction under different conditions were followed by estimating precipitated calomel at different time intervals by a volumetric estimation. Products of oxidation were separated by TLC and identified by standard spot tests[7,8].

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 induction period falls with increase of temperature and fructose concentration (Tables 1 and 2).

TABLE 1
VARIATION OF INDUCTION PERIOD WITH TEMPERATURE
$(HgCl_2)_0$ = 0.02 M, (Fructose) = 0.5M, $(KMnO_4)$ = 0.02 N

Temperature in °C	60	70	99.5
Induction period in mins	10	5	3

TABLE 2
VARIATION OF INDUCTION PERIOD WITH INITIAL FRUCTOSE
$(HgCl_2)_0$ = 0.02M, $(KMnO_4)$ = 0.02N, Temp. = 60°C

Fructose	0.02 M	0.04 M	0.05 M	0.5 M	1.0 M
Induction period in mins	130	100	90	10	4

A typical set of kinetics is recorded in Table 3 showing rate variation with time.

TABLE 3
$(HgCl_2)_0$ = 0.02 M, $(Fructose)_0$ = 0.5 M, $(KMnO_4)_0$ = 0.02 M, Temp. = 60° ± 0.1°C

Time (mins)	X KIO_3 (ml)	C = (a – x) KIO_3 (ml)	Hg(I) chloride (moles 1)	10^5 R (moles l^{-1} min^{-1})
0	0.00	20.00	0.00×10^{-3}	–
15	2.50	17.50	1.250	8.333
30	3.70	16.30	1.850	4.000
60	5.30	14.70	2.650	1.333
120	7.05	12.95	3.525	1.458
180	7.90	12.10	3.950	0.708
240	8.70	11.80	4.350	0.666
300	9.00	11.00	4.508	0.250
360	9.25	10.75	4.625	0.208

Similar kinetics were performed with same concentrations at different temperatures. It may be inferred that the overall reaction velocity increases with the rise in temperature. In order to ascertain the rate law, the reaction kinetics were followed with different initial concentrations of fructose, Hg(II) chloride and permanganate keeping other parameters constant. The reaction kinetics were studied at 60°C and the results are recorded in Table 4.

Scrutiny of the data in the above table shows that the reduction rate is fractional and can be expressed as:

$$d(Hg_2Cl_2)/dt = K(Fr.)^{0.4}\ K(Hg(II))^{0.3}\ K(MnO_4)^{0.6}$$

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

TABLE 4
VARIATION OF IR WITH INITIAL CONCENTRATIONS

Temperature = 60°C ± 0.1°C

(a) $(HgCl_2)_0 = 0.02M$, $(HgCl_2)_0 = 0.02N$

(b) $(Fructose)_0 = 0.5M$, $(KMnO_4)_0 = 0.02N$

(c) $(Fructose)_0 = 0.5M$, $(HgCl_2)_0 = 0.02M$

[Fructose] M	105 Av.R	$\frac{10^5 R}{(Fr.)^{0.4}}$	$(HgCl_2)_0$ M	10^5 R	$\frac{10^5 R}{(HgCl_2)^{0.3}}$	$[KMnO_4]$ N	10^5 R	$\frac{10^4 R}{(KMnO_4)^{0.6}}$
0.04	0.829	3.0	0.005	1.774	8.7	0.005	1.19	2.8
0.05	0.901	3.0	0.01	2.500	9.5	0.01	1.83	2.9
0.10	1.246	3.1	0.02	2.708	8.7	0.02	2.70	2.8
0.50	2.311	3.0	0.04	3.382	8.9	0.04	4.05	2.8
1.00	3.119	3.1	0.05	3.548	8.7	0.05	4.65	2.8

TABLE 5
OXIDATION PRODUCTS

Volatile	Non-volatile	Gaseous
Formaldehyde	D-Arabinoic,	Carbon dioxide
Formic acid	Glycollic, Oxalic acid and MnO_2	

It may be inferred that fructose on oxidation by neutral permanganate yields a variety of products which leads one to conclude that C_5, C_2 and C_1 compounds are produced in the fructose 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 below:

Mechanism

Chain Initiation Sequence:

$$MnO_4^- + H_2O = MnO_4^{2-*} + OH^{\cdot} + H^+ \qquad (1)$$

Chain Propagation Sequence:

$$CH_2OH(CHOH)_3COCH_2OH + OH^{\cdot} = CH_2OH(CHOH)_3CO\dot{C}HOH + H_2O \qquad (2)$$

$$CH_2OH(CHOH)_3COCH_2OH + MnO_4^- = CH_2OH(CHOH)_3CO\dot{C}HOH + MnO_3^- + OH^{\cdot} \qquad (3)$$

$$CH_2OH(CHOH)_3CO\dot{C}HOH \begin{array}{l} \xrightarrow{OH^{\cdot}} CH_2OH(CHOH)_3^- + CH_2O + CO_2^- + H^+ \qquad (4a) \\ \xrightarrow{OH^{\cdot}} \underset{\text{D-arabionic acid}}{CH_2OH(CHOH)_3COOH} + CH_2O \qquad (4b) \end{array}$$

$$CO_2^- + MnO_4^- = CO_2 + MnO_4^{2-*} \qquad (5)$$

$$CO_2^- + Hg(II) = CO_2 + Hg(I) \qquad (6)$$

Chain Termination Sequences

$$2OH^{\cdot} \rightarrow H_2O_2 \rightarrow H_2O + O \qquad (7)$$

$$CO_2^- + O_2 = CO_2 + O_2^- \qquad (8)$$

$$O_2^- + H^+ = HO_2 \text{ (leading to } H_2O_2) \qquad (9)$$

$$MnO_3^- + H^+ = MnO_2 + OH^{\cdot} \qquad (10)$$

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

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

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 C_1–C_2 bond by OH˙ 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 C_2–C_3 bond. Under such circumstances, erythrose could be the 4-carbon atom compound produced, the tentative mechanism of which is as follows:

$$\mathrm{CH_2OH(CHOH)_3COCH_2OH + OH^{\cdot} = CH_2OH(CHOH)_3^- + \underset{\text{Glycollic acid}}{CH_2OHCOOH}} \quad (11)$$

$$\mathrm{CH_2OH(CHOH)_3^- + MnO_4^- = \underset{\text{D-erythrose}}{CH_2OH(CHOH)_2CHO} + MnO_3^- + OH^{\cdot}} \quad (12)$$

In presence of a limited supply of the oxidant an aldehyde can be a terminating step as revealed by the work of Vasudeva and Wasif[9]. 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 reactions (4a) and (11) are the chain propagation sequences of the induced reduction reaction mechanism.

In consistency with this proposed mechanism, we report that

(i) Permanganate disproportionates at a much faster rate as a result of the reactions (1), (3) and (5).

(ii) The pH of the system remains steady with time due to the sequence reactions (1), (4), (8), (9) and (10).

(iii) Evolution of CO_2, identification of glycollic acid and formaldehyde indicate the degradation of fructose molecule and supports the above steps.

(iv) 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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