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Determination of Formic Acid and Formaldehyde Formed by Oxidation of Fructose by Potassium Peroxydisulphate

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The amounts of formic acid and formaldehyde formed as result of oxidation of a D (–) fructose molecule by potassium peroxydisulphate [$S_2O_8^{2-}$] were estimated. The values estimated were confirmed by the mechanism of the reaction through analysis of the redox reaction products which revealed the presence of formaldehyde and formic acid.

Key Words: Potassium peroxydisulphate, Formic acid, Formaldehyde, Oxidation, Fructose.

INTRODUCTION

In present studies, it is proposed to determine the amounts of formic acid and formaldehyde formed during oxidation of fructose by $S_2O_8^{2-}$. The amounts of unreacted D (–) fructose and the amounts of formaldehyde formed were determined spectrophotometrically[1,2] while that of formic acid formed was determined titremetrically[3].

EXPERIMENTAL

All chemicals used were AnalaR grade. All the solutions were prepared according to the usual analytical procedures using deionized water. Since the redox reaction of peroxydisulphate with organic compounds is highly susceptible to impurities in the solutions mainly chloride ions[4].

Analysis of the reaction products: A mixture of fructose (25 g) and potassium peroxydisulphate (25 g) in water (250 mL) was refluxed for 5 d at 60 ºC, until peroxydisulphate was used up. At the end of the reaction, the reaction mixture was evaporated to dryness under reduced pressure. The volatile fraction was taken for further analysis to identify the presence of formaldehyde and formic acid by spot tests[1,5]:

(A) Spectrophotometric estimation of formaldehyde: A solution containing small amount of formaldehyde when heated with sulphuric and chromotropic acids gives rise to a purple coloured complex[6] with maximum absorption at 580 nm. The absorbance of different solutions were found to be linear in formaldehyde concentration.

To 1 mL portions of series of solutions a, b, c, d, e and f [(taken in different flasks)], 10 mL of chromotropic acid solution was added and allowed to stand in water bath (90-98 ºC) for 0.5 h. The solutions were then left to cool to room temperature and their absorbance were determined at 580 nm using Perkin-Elmer UV/Vis spectrophotometer model 550S. Results are given in Table-1 from which the unknown amount of formladehyde was determined.

TABLE-1
ABSORBANCE OF THE STANDARD FORMALDEHYDE SOLUTIONS WITH SULPHURIC AND CHROMOTROPIC ACIDS

Solutions	10^4 concentration (mol/L)	Absorbance at 580 nm
a	5	0.432
b	10	0.959
c	15	1.382
d	20	1.748
e	25	2.225
f	30	2.663

(B) Spectrophotometric estimation of D(–) fructose: A set of standard D (–) fructose solutions were prepared and 2 mL portion of each solution was mixed with 8 mL of the anthrone reagent (0.2 % solution of anthrone in conc. sulphuric acid (98 %, 8 h old)[2] in different tubes. The mixtures were left to cool and after 10 min they were immersed in a cold water bath. A green colour developed due to the formation of arabinose-anthrone complex. The absorbance of each solution was determined at 620 nm using Perkin-Elmer spectrophotometer model 550S. Results are given in Table-2.

TABLE-2
ABSORBANCE OF THE STANDARD D(–) FRUCTOSE SOLUTIONS WITH ANTHRONE

Solutions	10^4 [Fructose] (mol/L)	Absorbance at 620 nm
S_1	1.00	0.112
S_2	3.00	0.331
S_3	5.00	0.543
S_4	7.00	0.751
S_5	9.00	1.050
S_6	10.00	1.101

Titmetric estimation of formic acid: It was determined by titration against 0.01 N NaOH using phenolphthalein as indicator[3].

Stoichiometry: For a stoichiometric study of the redox reaction. The reaction mixtures in the molar ratio $[S_2O_8^{2-}]$/[fructose], 1:1 to 1:8 were used. They were prepared in a total volume of 250 mL by deionized water and they had the following compositions:

Solution	$[S_2O_8^{2-}]$ (mol/L)	[Fructose] (mol/L)
A	0.004	0.004
B	0.004	0.008
C	0.004	0.012
D	0.004	0.016
E	0.004	0.020
F	0.004	0.024
G	0.004	0.032

The above reaction mixtures were refluxed for about 5 d until all peroxydisulphate was used up.

Estimation of the amount of unreacted D(–) fructose in the redox reaction: At the end of the redox reaction in the mixtures A to G , 4 mL of each reaction mixture were diluted to 100 mL in which 2 mL portions were analyzed for the unreacted D(–) fructose by the addition of the anthrone reagent as mentioned above in (**A**). Unknown amounts of D(–) fructose were determined with the help of these data. Results are given in Table-3.

TABLE-3
ESTIMATION OF UNREACTED FRUCTOSE

Solution	10^4 $[S_2O_8^{2-}]$ (mol/L)	10^4 $[\text{Fructose}]_o$ (mol/L)	Absorbance at 620 nm	10^4 [Fructose un reacted] (mol/L)	10^4 $[\text{Fructose oxidized}]_{ox}$ (mol/L)	$\frac{[\text{Fructose}]_{ox}}{[S_2O_8^{2-}]}$
A	1.60	1.60	0.130	1.07	0.53	0.331
B	1.60	3.20	0.240	2.37	0.83	0.519
C	1.60	4.80	0.431	3.75	1.05	0.656
D	1.60	6.40	0.532	4.97	1.43	0.894
E	1.60	8.00	0.691	6.27	1.73	1.081
F	1.60	9.60	0.852	6.70	2.90	1.813
G	1.60	12.80	0.050	9.70	3.10	1.938

Estimation of the amount of formaldehyde formed in the redox reaction: At the end of the redox reaction in the mixtures C, D, E and F. One mL portion of each was taken in different tubes and were analyzed for the amount of formaldehyde formed by the addition of 10 mL chromotropic acid reagent as mentioned above in (**B**). Results are given in Table-4.

TABLE-4
AMOUNTS OF FORMALDEHYDE FORMED IN THE REACTION MIXTURES C, D, E AND F

Solution	Absorbance at 580 nm	10^4 [HCHO] (mol/L)	10^4 [HCHO] (mol/ 250 L) reaction mixture
C	0.116	1.290	0.3226
D	0.164	1.818	0.4545
E	0.239	2.654	0.6635
F	0.322	3.572	0.8929

Estimation of the amount of formic acid formed in the redox reaction: At the end of the redox reaction in the mixtures C, D, E and F. The amounts of formic acid formed in each mixtures were determined by the titration of 10 mL portions of each against 0.01 N NaOH using phenolphthalein as indicator. Results are shown in Table-5.

TABLE-5
AMOUNTS OF FORMIC ACID FORMED IN THE REACTION MIXTURES C, D, E AND F

Solution	Titre 0.01 N NaOH mL	10^4 [HCHO] (mol/ 250 L) reaction mixture
C	0.80	2.000
D	1.00	2.500
E	1.25	3.125
F	1.75	4.375

RESULTS AND DISCUSSION

The linear plots pass through the origin at formaldehyde and fructose concentration respectively, show that the systems obey Beer's law and can be studied spectrophotometrically.

The linear plot was used to find out the amounts of formaldehyde formed in the diluted reaction mixtures C, D, E and F (Table-4), while the linear plot was used to find out the amounts of unreacted fructose in the diluted reaction mixtures A to G (Table-3).

When $[\text{fructose}]_{ox}$ oxidized per mole of peroxydisulphate was plotted against the initial concentration of fructose, $[\text{fructose}]_o$ a straight line, passing through the origin was obtained. This result shows that:

$$\frac{[\text{Fructose}]_{ox}}{[S_2O_8^{2-}]} = K[\text{Fructose}]_o$$

The order of this reaction in peroxydisulphate concentration was found to be unity[8]. The stoichiometric equation can be written as follows:

$$S_2O_8^{2-} + n \text{ fructose} \longrightarrow \text{oxidized fructose}$$

The value of n in the above equation should give the order of the reaction with respect to fructose concentration which represents the slope of the plot of fructose oxidized, $[\text{fructose}]_{ox}$ against the initial concentration of fructose, $[\text{fructose}]_o$ which was also linear.

According to the proposed mechanism of the redox reaction between potassium peroxydisulphate and D(–) fructose[6].

The following scheme was designed to show the formation of products:

$$CH_2OHCO(CHOH)_3CH_2OH + OH \rightarrow CH_2OHCO(CHOH)_3CHOH + H_2O$$

$$CH_2OHCO(CHOH)_3CHOH \rightarrow CH_2OHCO(CHOH)_3 + \underline{HCHO}$$

$$CH_2OHCO(CHOH)_3 + SO_4 \rightarrow CH_2OHCO(CHOH)_2 + \underline{CHO} + HSO_4$$

$$CH_2OHCO(CHOH)_2 + SO_4 \rightarrow CH_2OHCO(CHOH) + \underline{CHO} + HSO_4$$

$$CH_2OHCO(CHOH) + SO_4 \rightarrow CH_2OHCO + \underline{CHO} + HSO_4$$

$$CH_2OHCO + SO_4 \rightarrow \underline{2CHO} + HSO_4$$

This scheme gives rise to five CHO radicals which give rise to formic acid as follows:

$$5CHO + 5\ OH^{\bullet} \rightarrow 5HCOOH.$$

This scheme should finally leads to the formation of 5 molecules of formic acid and one molecule of formaldehyde for each molecule of oxidized fructose, the ratio of [HCHO]/[HCOOH] is expected to be 1:5, it is however found that it falls between 1:4.9 to 1:6.2. Results are shown in Table-6, the slight difference probably due to the tendency of formaldehyde to be oxidized to formic acid.

TABLE-6
RATIO OF FORMALDEHYDE TO FORMIC ACID [HCHO]/[HCOOH] FORMED IN THE REACTION MIXTURES C, D, E AND F

Solution	10^4 [HCHO] mole	10^4 [HCOOH] mole	$\frac{[HCHO]}{[HCOOH]}$
C	0.3226	2.000	1:6.2
D	0.4545	2.500	1:5.5
E	0.6635	3.125	1:4.7
F	0.8929	4.375	1:4.9

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