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A stoichiometric study on the uncatalysed reaction between potassium peroxydisulphate and L(-)arabinose

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ABSTRACT: A stoichiometric study on the uncatalysed redox reaction between potassium peroxydisulphate abbreviated in this paper as **[$S_2O_8^{=}$]** and L (-) arabinose was attempted according the analysis of the redox reaction products which revealed the presence of formaldehyde and formic acid in the volatile fraction , while the non- volatile fraction consisted mainly of potassium hydrogen sulphate , unreacted L (-) arabinose and other products of oxidation.[1] The amounts of unreacted L (-) arabinose and the amounts of formaldehyde formed were determined spectrophotometrically , while that of formic acid formed was determined titremetrically.

EXPERIMENTAL:

All chemicals used were AnalaR grade. All 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.[2]

Analysis of the reaction products:

A mixture of arabinose (25g) and potassium peroxydisulphate (25g) in water (250ml) was refluxed for 5 days at 60°, until peroxydisulphate was used up. A reflux condenser was used in which cold water (10C°) circulated throughout the heating in order to prevent the escaping of the volatile products. At the end of the reflux, the reaction mixture was evaporated to dryness under reduced pressure. The volatile fraction (resulting distillate) was taken for further analysis to identify the presence of formaldehyde and formic acid by **spot tests** as follows:

Formaldehyde :

To ½ ml of the resulting distillate was added 2 ml concentrated sulphuric acid and 2ml chromotropic acid in a test tube. The mixture was heated for 10 minutes on a water bath at 60 C°. A violet colour was developed indicating the presence of formaldehyde. To confirm the presence of formaldehyde, its **2,4 dinitrophenyl hydrazone** derivative was prepared by adding **2,4 dinitrophenyl hydrazine** to fraction of distillate, when recrystallized from ethanol gave a m.p. 166-167 C.°[3]

Formic Acid :

To 2 ml of the resulting distillate, 1 ml of $HgCl_2$ solution was added and the mixture was heated. A white precipitate turning to grey-black was obtained indicating the presence of formic acid. To confirm the presence of formic acid , its **amide** derivative was prepared by adding 2 ml of the distillate to 1g of PCl in a porcelain basin. The contents were mixed thoroughly until the mixture became liquid, then 20 ml of NH_4OH solution were added drop by drop. The mixture was then filtered and washed with cold water. The derivative was recrystallized from water and dried, gave a m.p. 194-195 C° which was the same with the pure derivative.[3]

(A) Spectrophotometric estimation of formaldehyde (the standard calibration curve) :

A solution containing very small amount of formaldehyde when heated with sulphuric and chromotoropic acids gives rise to a purple coloured complex with maximum absorption at 580nm.[4]

The absorbance of different solutions were found to be linear in formaldehyde concentration.[5]

To one 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 – 98C°)) for 30 minutes. The solutions were then left to cool to room temperature and their absorbance were determined at 580nm using Perkin-Elmer uv/vis spectrophotometer model 550S**.** Results are given in **table** (**1**) and graphically represented by **figure** (**2.1**)**.** Unknown amounts of formaldehyde were determined with the help of **figure** (**2.1**)**.**

(B) Spectrophotometric estimation of L (-) arabinose (the standard calibration curve) :

A set of standard L (-) arabinose 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 hours old))**.**[6] in different tubes. The mixtures were left to cool and after 10 minutes 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)** and graphically represented in **figure (4.A.11).**

(C) Titmetric estimation of formic acid: It was determined by titration against 0.01 N NaOH using phenolphthalein
as indicator.[7]

Stoichiometry:

For a stoichiometric study of the redox reaction, The reaction mixtures in the molar ratio $[S_2O^{=}_8]$/[Arabinose], 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**:**

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

Estimation of the amount of unreacted L(-)arabinose in the redox reaction :

At the end of the redox reaction in the mixtures **A** to **G ,** 4ml of each reaction mixture were diluted to 100 ml in which 2 ml portions were analysed for the unreacted L (-) arabinose by the addition of the anthrone reagent as mentioned above in**(A).**Unknown amounts of L (-) arabinose were determined with the help of **figure** (**4.A.11**)**.** Results are given in **table (3).**

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 . 1** ml portion of each was taken in different tubes and were analysed 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).**

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 0.01N NaOH using phenolphthalein as indicator**.** Results are shown in **table (5).**

Solution	$[S_2O^{=}_8]$ mole/l	[Arabinose] mole/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

RESULTS AND DISCUSSTOIN :

Table(1): Absorbance of the standard formaldehyde solutions with sulphuric and chromotoropic acids:

Solutions	10^4 concentration Mole/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

TABLE (2)::Absorbance of the standard L(-) arabinose solutions with anthrone

Solutions	10^4 [Arabinose] Mole/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

The linear plots obtained in **figures (2.1)** and **(4.A.11)** which pass through the origin at formaldehyde and arabinose concentration respectively, show that the systems obey Beer's law and can be studied spectrophotometrically**.** The linear plot of **figure (2.1**) 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 of **figure (4.A.11)** was used to find out the amounts of unreacted arabinose in the diluted reaction mixtures **A** to **G table(3).**

When $[Arabinose]_{ox}$ oxidized per mole of peroxydisulphate was plotted against the initial concentration of arabinose,$[Arabinose]_o$ a straight line, passing through the origin was obtained, **figure (4.A.12)**, this result shows that:

$$\frac{[Arabinose]_{ox}}{[S_2O^{=}_8]} = K\,[Arabinose]_o$$

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

$S_2O^{=}_8$ + **n** arabinose ⟶ oxidized arabinose

The value of **n** in the above equation should give the order of the reaction with respect to arabinose concentration which it represent the slope of the plot of arabinose oxidized, $[Arabinose]_{ox}$ against the initial concentration of arabinose, $[Arabinose]_o$ which was also linear **figure (4.A.13).**

TABLE (3): Estimation of unreacted arabinose:

Solution	$10^4[S_2O^{=}_8]$ mole/l	10^4[Arabinose]$_o$ mole/l	Absorbance at 620 nm	10^4[Arabinose un reacted] mole/l	10^4[Arabinose oxidized]ox mole/l	$\frac{[Arabinose]_{ox}}{[S_2O^{=}_8]}$
A	1.60	1.60	0.173	1.57	0.03	0.019
B	1.60	3.20	0.288	2.61	0.59	0.369
C	1.60	4.80	0.375	3.40	1.40	0.875
D	1.60	6.40	0.439	3.98	2.42	1.513
E	1.60	8.00	0.477	4.33	3.67	2.294
F	1.60	9.60	0.593	5.38	4.22	2.638
G	1.60	12.80	0.675	6.13	6.67	4.168

TABLE (4): Amounts of formaldehyde formed in the reaction mixtures C,D.E and F.

Solution	Absorbance At 580nm	10^4[HCHO] mole/l	10^4[HCHO] mole /250ml reaction mixture
C	0.673	7.4667	1.8667
D	0.874	9.6939	2.4235
E	0.986	10.9264	2.7316
F	1.184	13.1222	3.2805

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[HCOOH] mole/ 250 ml reaction mixture
C	0.70	7.00
D	0.95	9.50
E	1.15	11.50
F	1.45	14.50

According to the proposed mechanism of the redox reaction between potassium peroxydisulphate and L(-) arabinose [8]
The following scheme was designed to show how such products can be formed:-

$$CHO.(CHOH)_3.CH_2OH + OH \longrightarrow CHO.(CHOH)_3CHOH + H_2O$$

$$CHO.(CHOH)_3.CHOH \longrightarrow CHO.(CHOH)_3 + \underline{HCHO}$$

$$CHO.(CHOH)_3 + SO_4 \longrightarrow CHO(CHOH)_2 + CHO + HSO_4$$

$$CHO.(CHOH)_2 + SO_4 \longrightarrow CHO.(CHOH)+CHO+HSO_4$$

$$CHO.(CHOH) + SO_4 \longrightarrow 2CHO + HSO_4$$

This scheme gives rise to four **CHO** radicals which give rise to formic acid as follows:-

$$4\,CHO + 4\,OH^{\cdot} \longrightarrow \underline{4HCOOH} \quad . \quad (22)$$

This scheme should finally leads to the formation of four molecules of formic acid and one molecule of formaldehyde for each molecule of oxidized arabinose, the ratio of **[HCHO] / [HCOOH]** is expected to be **1:4**, it is however found that it falls between 1**:**3.7 to 1**:** 4.4**.** Results are shown in **table (6)**, the slight difference probably due to the tendency of formaldehyde to be oxidized to formic acid**.**

TABLE (6): The ratio of formaldehyde to formic acid [HCHO] / [HCOOH] formed in the reaction mixtures C,D.E and F.

Solution	**10^4[HCHO] mole/l**	**10^4[HCOOH] mole/l**	**$\frac{[HCHO]}{[HCOOH]}$**
C	1.8667	7.00	1**:**3.7
D	2.4235	9.50	1**:**3.9
E	2.7316	11.50	1**:**4.2
F	3.2805	14.50	1**:**4.4

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