

Thermodynamic Parameters of the Uncatalyzed Redox Reaction Between Potassium Peroxydisulphate and D(+)Glucose

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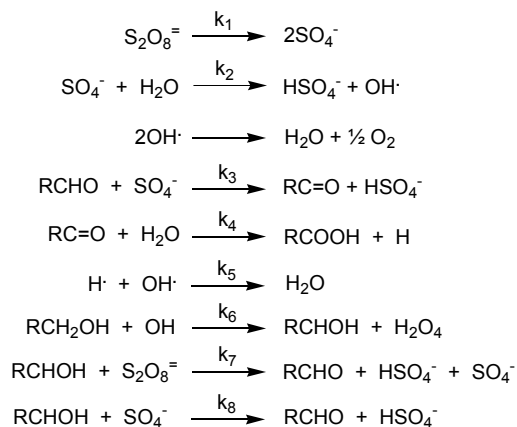
Abstract

The uncatalyzed redox reaction between potassium peroxydisulphate and D(+) glucose was studied titrimetrically . The progress of the reaction was followed by examining the concentration of potassium peroxydisulphate in the reaction mixture at different time intervals by iodometric titration method. Thermodynamic parameters, activation energy (E_a), frequency factor (A), entropy change (ΔS) and the free energy change (ΔG) of the uncatalyzed redox reaction were evaluated from the values of the fractional order rate constants k_o at different temperatures.

Keywords: Uncatalyzed redox reaction, thermodynamic parameters, D(+)glucose, Potassium peroxydisulphate.

1. Introduction

The readily available peroxydisulphate ion, $[S_2O_8^{2-}]$ is an excellent and versatile oxidant for a variety of organic and inorganic compounds (Bacon et al. 1966; Menghani & Bakore 1998). The oxidation of some carbohydrates such as sucrose, rhamnose and dextrose were studied earlier by Wood & Walker 1914. Vasudeva in 1969 studied the uncatalyzed oxidation of D(+)glucose by peroxydisulphate and found the reaction follow first order in peroxydisulphate ion and fractional order in glucose, he proposed the following mechanism;



The decomposition of peroxydisulphate takes place as a result of the symmetric cleavage of the o – o bond of the peroxydisulphate ion to make two sulphate free radicals ($SO_4^{\cdot -}$) (Kolthoff & Miller 1951). The sulphate free radical disappear either by reaction with water to produce oxygen or by reaction with glucose molecule to give free radical which attack peroxydisulphate and this explain the increase in the rate of decomposition of peroxydisulphate by the addition of glucose. The kinetic measurements were carried out over the temperature range 60–80 °C. Since the

reaction does not take place to any measurable extent at room temperature ($t_{1/2}$ = one month) (Vasudeva 1969).

2. Experimental

All chemicals used were AnalaR grade. All solutions were prepared according to the usual analytical procedures. Deionized water was used in all kinetic runs. The iodometric method was used for the analysis and estimation of unreacted peroxydisulphate $[S_2O_8^{2-}]$ which is a modification of the method used by Bartlett & Cottman in 1949 and Rosin in 1946.

3. Results and Discussion

Tables (1) to (5) include the results of the kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature range of 60-80 °C in which the initial concentration of peroxydisulphate and D(+) glucose at zero time of the reaction was 0.02 mol dm^{-3} .

Table 1. kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature 60 °C.

Time, s	Titre, mL	$10^3 [S_2O_8^{2-}]$, mol dm^{-3}	$3 + \log [S_2O_8^{2-}]$
0	9.60	20.000	1.3010
2400	5.10	10.625	1.0263
4800	3.60	7.500	0.8751
7200	2.80	5.833	0.7659
9600	2.00	4.167	0.6198
12000	1.60	3.333	0.52228
14400	1.20	2.500	0.3979

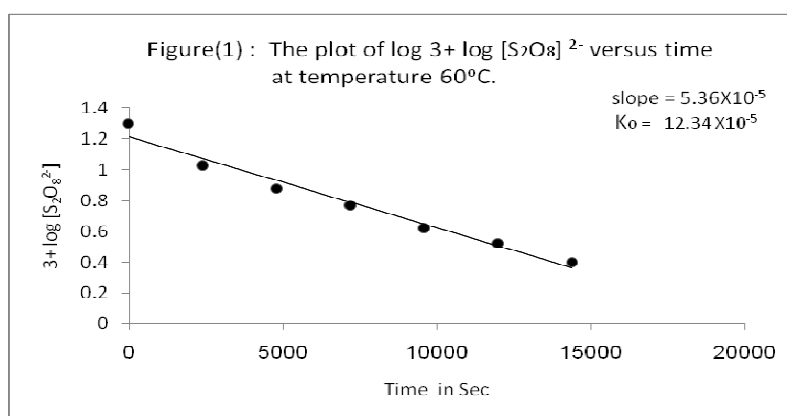


Table 2. kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature 65 °C.

Time, s	Titre, mL	$10^3 [S_2O_8^{2-}]$, moldm ⁻³	$3+ \log [S_2O_8^{2-}]$
0	8.20	20.000	1.3010
1800	6.20	15.122	1.1796
3600	3.60	8.780	0.9435
5400	1.90	4.634	0.6600
7200	1.50	3.659	0.5634

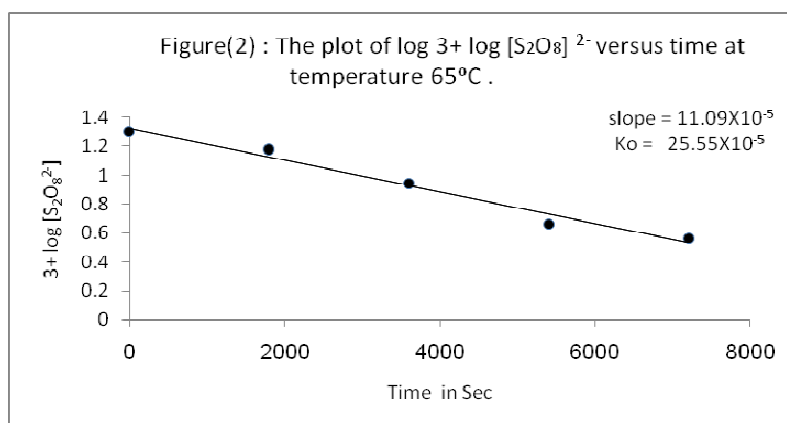


Table 3. kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature 70 °C.

Time, s	Titre, mL	$10^3 [S_2O_8^{2-}]$, moldm ⁻³	$3+ \log [S_2O_8^{2-}]$
0	7.95	20.000	1.3010
1800	4.90	12.3270	1.09086
3600	3.10	7.7987	0.89202
5400	1.80	4.5283	0.65594
7200	1.20	3.01887	0.4784

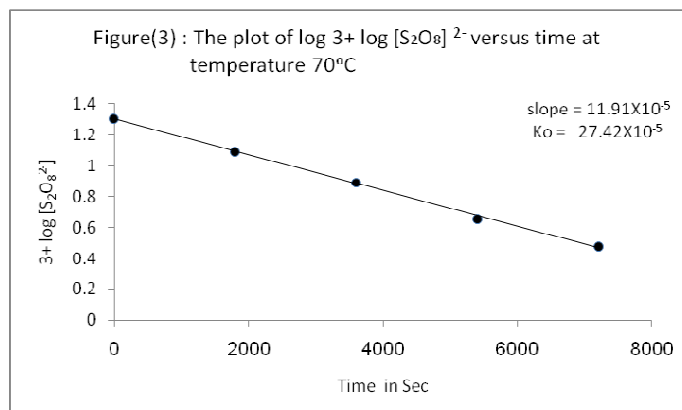


Table 4. kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature 75°C.

Time, s	Titre, mL	$10^3 [S_2O_8^{=}]$, moldm ⁻³	$3+ \log [S_2O_8^{=}]$
0	9.30	20.000	1.3010
1200	4.70	10.108	1.0047
2400	2.60	5.591	0.7475
3600	1.30	2.796	0.44465

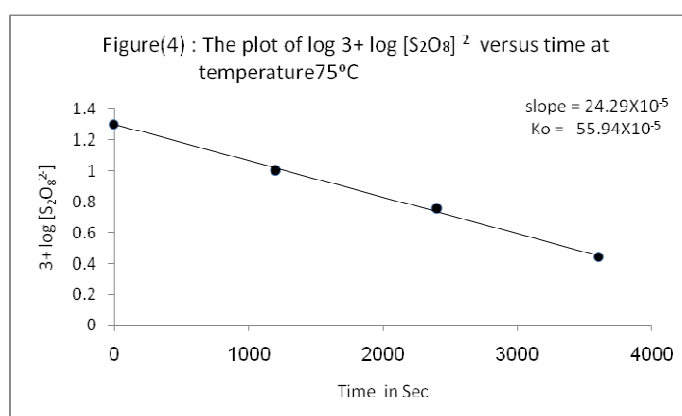
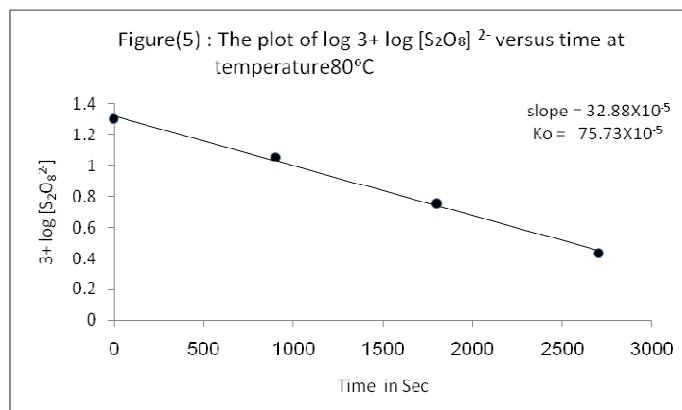


Table 5. kinetic measurements of the redox reaction between potassium peroxydisulphate and D(+) glucose at a temperature 80°C.

Time, s	Titre, mL	$10^3 [S_2O_8^{=}]$, moldm ⁻³	$3+ \log [S_2O_8^{=}]$
0	8.10	20.000	1.3010
900	4.60	11.3580	1.05530
1800	2.30	5.6790	0.7543
2700	1.10	2.7160	0.43394



The first order observed rate constant k_o was estimated by the integrated rate law as follows:

$$k_o = \frac{2.303}{t} \log \frac{[S_2O_8^-]_o}{[S_2O_8^-]}$$

where, $[S_2O_8^-]_o$ is the initial concentration of potassium peroxydisulphate at $t = \text{zero}$ and $[S_2O_8^-]$ is the concentration of potassium peroxydisulphate at $t = t$.

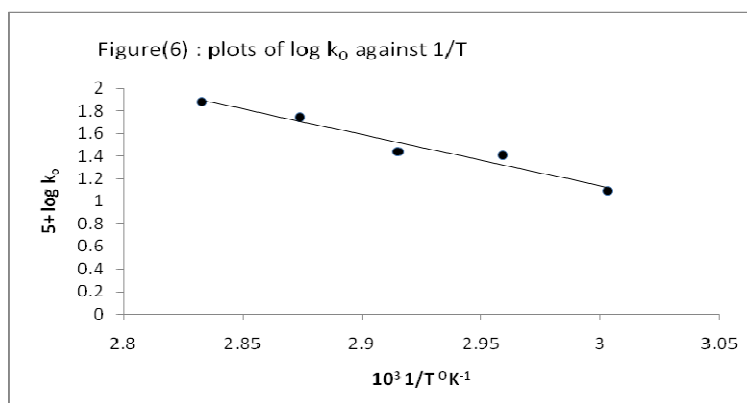
The above equation can be rewritten as follows:

$$\log \frac{[S_2O_8^-]_o}{[S_2O_8^-]} = \frac{k_o t}{2.303}$$

The plot of $\log [S_2O_8^-]_o/[S_2O_8^-]$ against time (t) will be a straight line in which its slope equals to $k_o/2.303$ from which k_o was calculated (Figures 1-5).

Table 6. Summary of Tables (1) to (5)

T, K	$10^3 1/T, K^{-1}$	$10^5 k_o s^{-1}$	$5 + \log k_o$
333	3.003	12.34	1.0913
338	2.959	25.55	1.4074
343	2.915	27.42	1.4381
348	2.874	55.94	1.7477
353	2.833	75.73	1.8793



From Table 6 the plots of $\log k_0$ against $1/T$ were linear and the activation energy (E_a) was calculated from the slope of the plot (Figure 6) by the equation:

$$E_a = - \text{slope} \times 2.303 \times R \quad \text{cal mol}^{-1}$$

The value of the frequency factor A (s^{-1}), was calculated from the intercept of the straight line with the y -axis. Further, the change in entropy ΔS and the change in the free energy ΔG were calculated by the following equations:

$$\Delta S = 2.303R (\log A - \log RT/Nh) \quad \text{JK}^{-1}$$

where R/N is the Boltzman's gas constant $1.3806 \times 10^{-23} \text{ JK}^{-1}$ and h is Plank's constant $6.62 \times 10^{-34} \text{ Js}^{-1}$.

$$\Delta G = \Delta E_a - T\Delta S \quad \text{KJ mol}^{-1}$$

Table 7. Thermodynamic parameters for glucose–peroxydisulphate reaction

Activation energy E_a in kcalmol ⁻¹	Frequency factor A in s ⁻¹	Free energy change ΔG in KJmol ⁻¹		Entropy change ΔS in calK ⁻¹	
34.72	158.49X10 ⁻³	60	12.553	60	-208.64
		65	13.640	65	-209.31
		70	14.730	70	-209.93
		75	15.822	75	-210.50
		80	16.918	80	-211.04

5. Conclusion

Since peroxydisulphate decomposes thermally even in the absence of a substrate, two main reaction paths were found (Abualreish, 2007), path (I) represents the thermal decomposition of peroxydisulphate alone in which the activation energy is 28.70 kcal/ mole and the frequency factor is $12.30 \times 10^{-5} \text{ sec}^{-1}$ (Abualreish, 2008) and path (II) represents the bimolecular reaction of peroxydisulphate with glucose as reducing agent the activation energy is 34.72 kcal/ mole and the frequency factor is $158.49 \times 10^{-3} \text{ sec}^{-1}$, which means that the present of a substrate increase the activation energy of thermal decomposition of potassium peroxydisulphate 6.02kcal/mole.

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