

# The Influences of Catalysts and Co-catalysts on the Thermal Decomposition of Potassium Peroxydisulphate in Aqueous Solution at 70 °C

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**Abstract** The thermal decomposition of potassium peroxydisulphate at 70°C under catalyzed conditions was investigated. The decomposition was catalyzed by different systems namely, the silver (I) ion, the copper (II) ion and in the presence of both ions (co- catalysts). It is obvious that the presence of small amount of silver(I) or copper (II) ion enhance the rate of decomposition of peroxydisulphate. A systematic kinetic study showed that the catalytic influence of the different systems used in the decomposition is in the following order :co-catalyst > Ag<sup>+</sup> > Cu<sup>2+</sup>.

**Keywords** Thermal Decomposition, Potassium Peroxydisulphate, Co-catalyst

## 1. Introduction

The thermal decomposition of potassium peroxydisulphate was the subject of study of many workers [1-3], they all suggested that the decomposition follows a first order kinetics. Early workers [4], studying the thermal decomposition of potassium peroxydisulphate found that the decomposition in aqueous solution was accelerated by rise of temperature and depends on the concentration of solution. Levr and Migliorini [5] have found that the thermal decomposition of potassium peroxydisulphate was unimolecular and is catalyzed by acid. The silver ion catalysed decomposition of peroxydisulphate ion was studied by Bawn and Margrerison [6], their studies showed that the decomposition is first order in both silver and peroxydisulphate ion. Abualreish [7] studied the uncatalyzed thermal decomposition of potassium peroxydisulphate. He found that the decomposition is first order in peroxydisulphate concentration and satisfies the relation :

$R = K_o[S_2O_8^{2-}]_o$  the value the observed rate constant  $k_o$  equal to  $0.54 \times 10^{-5} \text{ sec}^{-1}$ . Bartlett and Cottman [8] have suggested that the radicals produced in the Peroxydisulphate ion decomposition in aqueous solution cannot induce the decomposition of the ion and that autocatalysis is not observed in the thermal decomposition of peroxydisulphate.

## 2. Experimental

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All chemicals used were AnalaR grade. All solutions were prepared according to the usual analytical procedures. Deionized water was used in all kinetic runs. Since the reaction does not take place to any measurable extent at room temperature ( $t_{1/2}$  = one month) [9], the temperature used was 70 °C. 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 and Cottman [8] and Rosin [10]. In this method to 5 ml of the reaction mixture, 5 ml sodium bicarbonate and one ml of sulphuric acid were added to maintain a pH value of 7.1 to 7.2. The liberated iodine was titrated against sodium thiosulphate using starch as indicator.

## 3. Results and discussion

For many reducing agents, oxidation by peroxydisulphate does not proceed at a convenient rate at 25 °C, unless a catalyst is present. The most thoroughly investigated catalyst is the silver (I) ion [11], although reactions involving the copper (II) ion [12] and the iron (II) ion [13] also have been studied. Dependence of the rate of decomposition of peroxydisulphate on the systems:  $[Ag^+]$ ,  $[Cu^{2+}]$  and  $[Ag^+ + Cu^{2+}]$  : Tables (1), (2) and (3) show the catalytic effect of Ag(I), Cu(II) and  $[Ag(I) + Cu(II)]$  ions on the thermal decomposition of potassium peroxydisulphate at 70°C in which the concentration of Ag(I), Cu(II) and  $[Ag(I) + Cu(II)]$  ions varies from 0.01 to 0.1 mole/l while that of peroxydisulphate was kept constant at 0.01 mole/l. Results were represented graphically in figures (1) and (2) for Ag(I) ion, (3) and (4) for Cu(II) ion and (5) and (6) for  $[Ag(I) + Cu(II)]$  ion.

**Table 1.** Dependence of the rate of decomposition of peroxydisulphate on Ag(I) ion

[AgNO <sub>3</sub> ] <sub>0</sub> mole/l	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sub>Aver</sub> mole/l	10 <sup>6</sup> R mole/ l/sec	10 <sup>5</sup> k <sub>o</sub> sec <sup>-1</sup>
0.01	0.00884	0.3000	3.41
0.02	0.00861	0.4028	4.29
0.03	0.00819	0.4736	5.80
0.04	0.00742	0.6361	8.81
0.05	0.00686	0.8264	11.41
0.06	0.00652	0.8486	13.35
0.08	0.00580	0.9861	17.50
0.1	0.00516	1.1222	22.36

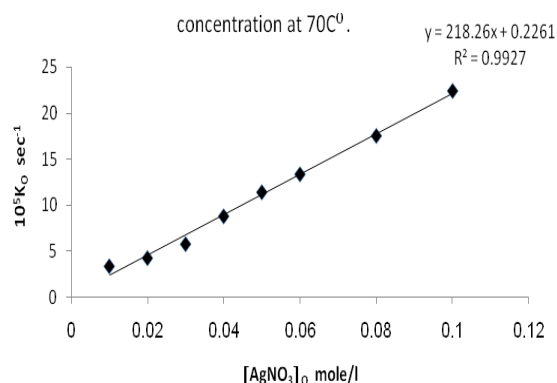
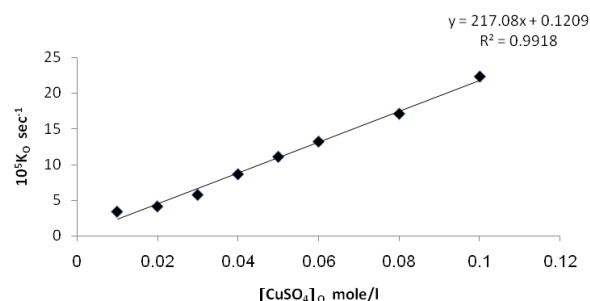
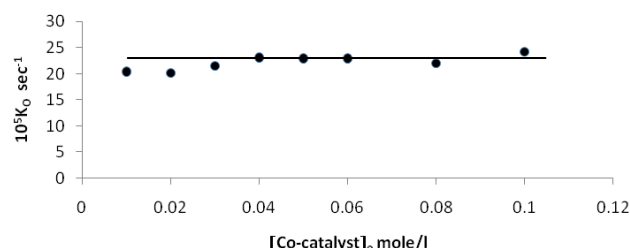
**Table 2.** Dependence of the rate of decomposition of peroxydisulphate on Cu(II) ion

[CuSO <sub>4</sub> ] <sub>0</sub> mole/l	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sub>Aver</sub> mole/l	10 <sup>6</sup> R mole/ l/sec	10 <sup>5</sup> k <sub>o</sub> sec <sup>-1</sup>
0.01	0.00885	0.2986	3.39
0.02	0.00868	0.3208	4.12
0.03	0.00820	0.4694	5.75
0.04	0.00745	0.6681	8.64
0.05	0.00693	0.8083	11.08
0.06	0.00655	0.8417	13.21
0.08	0.00586	0.8611	17.11
0.1	0.00514	0.9750	22.33

**Table 3.** Dependence of the rate of decomposition of peroxydisulphate on [Ag(I) + Cu(II)] ion

[AgNO <sub>3</sub> ] <sub>0</sub> = [CuSO <sub>4</sub> ] <sub>0</sub> mole/l	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sub>0</sub> mole/l	10 <sup>6</sup> R mole/ l/sec	10 <sup>5</sup> k <sub>o</sub> sec <sup>-1</sup>
0.01	0.00436	0.7073	20.39
0.02	0.00483	0.7167	20.17
0.03	0.00419	0.7312	21.48
0.04	0.00392	0.7750	23.11
0.05	0.00360	0.8135	22.94
0.06	0.00345	0.8260	22.96
0.08	0.00437	0.8813	22.06
0.1	0.00398	0.9219	24.20

Figures (1) and (3), show that the value of k<sub>o</sub> increases linearly with the increasing concentration of Ag(I) and Cu(II) ions respectively, indicating first order dependence of the reaction on the catalyst concentration. In the case of the system [Ag<sup>+</sup> + Cu<sup>2+</sup>] (figure (5)), the value of k<sub>o</sub> does not increase linearly with the increasing concentration of [Ag<sup>+</sup> + Cu<sup>2+</sup>]. It that means the value of k<sub>o</sub> is independent of the initial co-catalyst concentration.

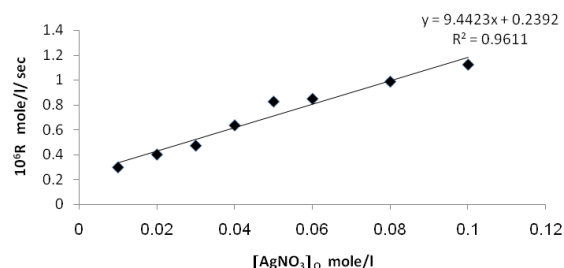
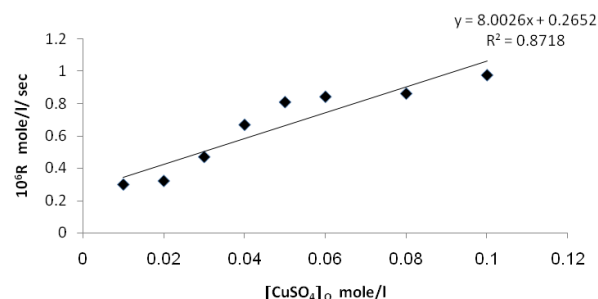
**Figure 1.** Observed rate dependence on Ag<sup>+</sup> ion concentration at 70 °C**Figure 3.** Observed rate dependence on Cu<sup>++</sup> ion concentration at 70 °C**Figure 5.** Plot of the observed rate constant k<sub>o</sub> against [Co-catalyst]<sub>0</sub> at 70 °C

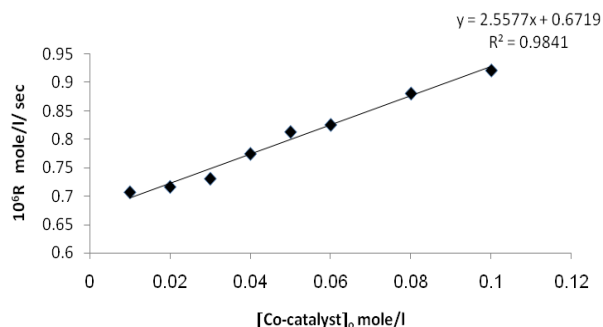
From figures (2), (4), and (6) the intercept at the rate axis is equal to 0.25X10<sup>-6</sup> mole/l/sec for Ag(I), 0.23X10<sup>-6</sup> mole/l/sec for Cu(II), and 0.67X10<sup>-6</sup> mole/l/sec for [Ag(I) + Cu(II)] ion. Therefore the observed first order rate law for the three systems can be expressed as follows:

$$R = 0.25 \times 10^{-6} + k_o [\text{Ag}^+]_0$$

$$R = 0.23 \times 10^{-6} + k_o [\text{Cu}^{2+}]_0$$

$$R = 0.67 \times 10^{-6} + k_o [\text{Ag}^+ + \text{Cu}^{2+}]_0$$

**Figure 2.** Rate dependence on Ag<sup>+</sup> ion concentration at 70 °C**Figure 4.** Rate dependence on Cu<sup>++</sup> ion concentration at 70 °C

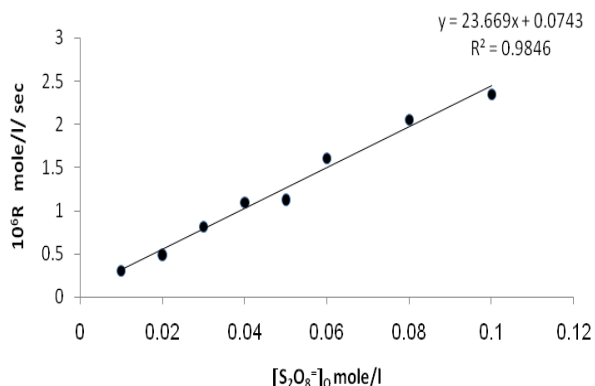


**Figure 6.** Plot of the rate R against  $[\text{Co-catalyst}]_0$  at 70 °C

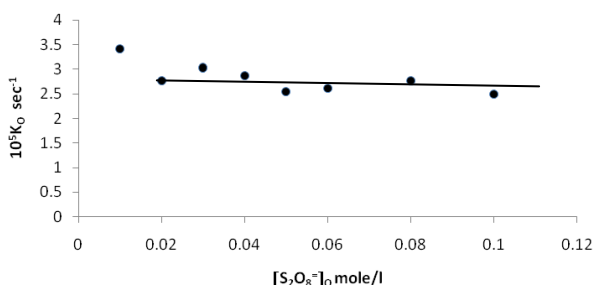
The reactions were also studied at various peroxydisulphate concentrations and constant  $[\text{Ag}^+]$ ,  $[\text{Cu}^{2+}]$  and  $[\text{Ag}^+ + \text{Cu}^{2+}]$  concentrations. Results are shown in tables (4), (5) and (6) and represented graphically in figures (7) and (8) for Ag(I) ion, (9) and (10) for Cu(II) ion and (11) and (12) for  $[\text{Ag(I)} + \text{Cu(II)}]$  ions.

**Table 4.** Peroxydisulphate dependence :  $[\text{AgNO}_3]_0 = 0.01 \text{ mole/l}$  Temp. 70 °C

$[\text{S}_2\text{O}_8^{2-}]_0$ mole/l	$[\text{S}_2\text{O}_8^{2-}]_{\text{Aver}}$ mole/l	$10^6 R$ mole/ l/sec	$10^5 k_0$ sec <sup>-1</sup>
0.01	0.00841	0.3000	3.41
0.02	0.01816	0.4847	2.76
0.03	0.02704	0.8111	3.03
0.04	0.03607	1.0958	2.86
0.05	0.04575	1.1264	2.54
0.06	0.05477	1.6069	2.61
0.08	0.07257	2.0542	2.76
0.1	0.0915	2.3459	2.49



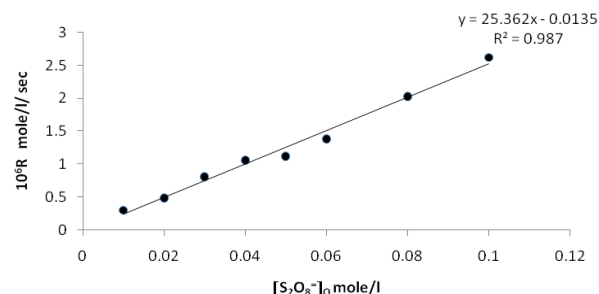
**Figure 7.** Rate dependence on  $[\text{S}_2\text{O}_8^{2-}]_0$  at 70 °C



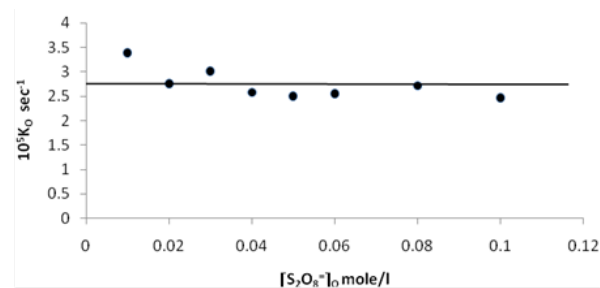
**Figure 8.** Plot of the observed rate constant  $K_0$  against  $[\text{S}_2\text{O}_8^{2-}]_0$  at 70 °C

**Table 5.** Peroxydisulphate dependence :  $[\text{CuSO}_4]_0 = 0.01 \text{ mole/l}$  Temp. 70 °C

$[\text{S}_2\text{O}_8^{2-}]_0$ mole/l	$[\text{S}_2\text{O}_8^{2-}]_{\text{Aver}}$ mole/l	$10^6 R$ mole/ l/sec	$10^5 k_0$ sec <sup>-1</sup>
0.01	0.00885	0.3000	3.41
0.02	0.01817	0.4847	2.76
0.03	0.02706	0.8111	3.03
0.04	0.03634	1.0958	2.86
0.05	0.04573	1.1264	2.54
0.06	0.05489	1.6069	2.61
0.08	0.07267	2.0542	2.76
0.1	0.07814	2.3459	2.49



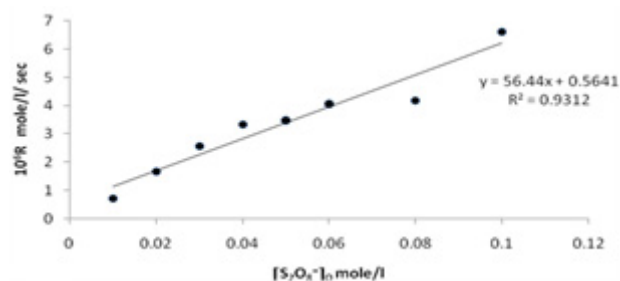
**Figure 9.** Rate dependence on  $[\text{S}_2\text{O}_8^{2-}]_0$  at 70 °C



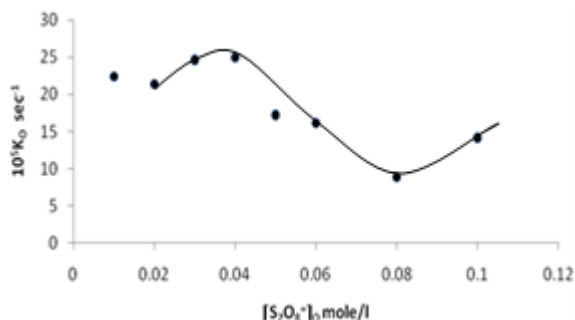
**Figure 10.** Plot of the observed rate constant  $K_0$  against  $[\text{S}_2\text{O}_8^{2-}]_0$  at 70 °C

**Table 6.** Peroxydisulphate dependence :  $[\text{AgNO}_3]_0 = [\text{CuSO}_4]_0 = 0.01 \text{ mole/l}$  Temp. 70 °C

$[\text{S}_2\text{O}_8^{2-}]_0$ mole/l	$[\text{S}_2\text{O}_8^{2-}]_{\text{Aver}}$ mole/l	$10^6 R$ mole/ l/sec	$10^5 k_0$ sec <sup>-1</sup>
0.01	0.00436	0.7073	22.39
0.02	0.00879	1.6521	21.36
0.03	0.01137	2.5573	24.59
0.04	0.01517	3.3283	24.89
0.05	0.02656	3.4719	17.23
0.06	0.03310	4.0438	16.12
0.08	0.05549	4.1667	8.90
0.1	0.05837	6.5969	14.14



**Figure 11.** Rate dependence on  $[\text{S}_2\text{O}_8^{2-}]_0$  at 70 °C



**Figure 12.** Plot of the observed rate constant  $k_0$  against  $[S_2O_8^{2-}]_0$  at 70 °C

Figures (7), (9), and (11) show the linearity of the initial peroxydisulphate concentration  $[S_2O_8^{2-}]_0$  with the rate ( $R$ ) for the three systems, so the rate can be expressed by the following equation:  $R = k_0[S_2O_8^{2-}]_0$ . Also, it is obvious from figures (8) and (10) that the relation is linear and parallel to the concentration axis giving a graphical mean of  $2.8 \times 10^{-5} \text{ sec}^{-1}$  in case of  $Ag^+$  ion and  $2.7 \times 10^{-5} \text{ sec}^{-1}$ , in case of  $Cu^{2+}$  ion. Therefore we conclude that the values of  $k_0$  were found to be independent of peroxydisulphate concentration, so the reaction is first order in  $[Ag^+]$  and  $[Cu^{2+}]$  and zero order in  $[S_2O_8^{2-}]$ . In the case of the system  $[Ag^+ + Cu^{2+}]$  (figure (12)), the relation is not linear and that means the order of the reaction with respect to peroxydisulphate is unknown.

**Table 7.**  $[S_2O_8^{2-}] = [Ag^+] = [Cu^{2+}] = [Ag^+ + Cu^{2+}] = 0.01 \text{ mole/l}$   
Temp 70 °C

	None(7)	$Cu^{2+}$	$Ag^+$	$Ag^+ + Cu^{2+}$
$10^6 R$ mole/ l/sec	0.2219	0.2986	0.3000	0.7073
$10^5 k_0$ sec <sup>-1</sup>	2.64	3.39	3.41	2.76

Table (7) includes a summary of the values of ( $R$ ) and ( $k_0$ ) for the catalytic and the co-catalytic thermal decomposition of potassium peroxydisulphate at 70 °C. The above findings

showed that the copper ion was much less efficient than the silver ion as catalyst for the thermal decomposition of peroxydisulphate. Finally, we can deduce that the catalytic influence of the different systems used in the thermal decomposition of peroxydisulphate is in the following order: co-catalyst >  $Ag^+$  >  $Cu^{2+}$ .

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