

The Inhibitory and Catalyzing Effects of Different Materials on the Thermal Decomposition of Potassium Peroxydisulphate in Aqueous Solution at 70 °C

M. J. A. Abualreish^{1,2}

¹ Department of Chemistry, Faculty of Science, Northern Borders University, Arar, Kingdom of Saudi Arabia (current address)

² Department of Chemistry, Faculty of Science and Technology, Omdurman Islamic University, Sudan (permanent address)

Correspondence: M. J. A. Abualreish, Department of Chemistry, Faculty of Science, Northern Borders University, Arar, Kingdom of Saudi Arabia. E-mail: Mustjeed_2008@hotmail.com

Received: January 17, 2012

Accepted: February 6, 2012

Online Published: May 27, 2012

doi:10.5539/ijc.v4n3p121

URL: <http://dx.doi.org/10.5539/ijc.v4n3p121>

Abstract

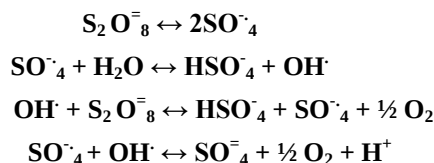
The present study is an investigation of the inhibitory effect of halides ions and the mineral salt potassium sulphate; and the catalyzing influences of electrolytes; non – electrolytes and the mineral salt mercuric chloride on the thermal decomposition of potassium peroxydisulphate at 70 °C. The study showed that the specific inhibitory effect of halides ions on the thermal decomposition is in the order: F < Cl < Br < I; while the catalyzing influences of electrolytes and non – electrolytes on the decomposition in the order: HCl > KCl > H₂SO₄ > K₂SO₄ > Urea. It was also found that potassium sulphate acts as an inhibitor on the thermal decomposition; while mercuric chloride exhibits a catalyzing influence on the decomposition.

Keywords: inhibitory effect, catalyzing influence, thermal decomposition, potassium peroxydisulphate

1. Introduction

The thermal decomposition of potassium peroxydisulphate was the subject of study of many workers (Morgan & Christ, 1927; Fronaeus & Ostman, 1955; Kolthoff & Miller, 1951), all they suggested that the decomposition follows a first order kinetics. Early workers (Green & Mason, 1910) 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. Levi and Migliorini (Levi, Migliorini, & Gazz, 1963) observed that peroxydisulphate solutions which were stable at 35 °C are decompose catalytically by the hydrogen and the hydroxyl ions as well as platinum black and lead. Fronaeus and Ostman (Fronaeus & Ostman, 1955) and Kolthoff and Miller (Kolthoff & Miller, 1951) showed that the rate constant of the decomposition was independent of the ionic strength but in acid solution there is a negative salt effect. Vasudeva (Vasudeva, 1969) noticed that in aqueous solution potassium peroxydisulphate decomposes slowly at 60 °C and the decomposition shows auto-inhibition in the beginning and then follows first order kinetics.

Bartlett and Cottman (1949) suggested for the uncatalyzed thermal decomposition the following chain mechanism:



Another mechanisms for the uncatalyzed thermal decomposition were suggested by Fronaeus and Ostman (1955) and Levitt (1953).

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. Since the reaction does not take place to any measurable extent at room temperature ($t_{1/2}$ = one month) (Vasudeva, 1969), 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 (Bartlett & Cotman, 1949) and Rosin (1946).

3. Results and Discussion

Tables (1) and (2) show the inhibitory effect of the metal halides, potassium chloride and potassium bromide on the thermal decomposition of potassium peroxydisulphate at 70 °C in which the concentration of the metal halides were 0.1 and 0.2 mole/l while that of peroxydisulphate was kept constant at 0.01 mole/l. Results were represented graphically in Figure (1).

Table 1. The inhibitory effect of the metal halides, potassium chloride and potassium bromide on the thermal decomposition of potassium peroxydisulphate at 70 °C

Time min	None	X ml	KCl 0.1M	X ml	KCl 0.2M	X ml	KBr 0.1M	X ml	KBr 0.2M	X ml
0	15.0		15.0		15.0		15.0		15.0	
20	13.7	1.3	14.8	0.2	14.7	0.3	14.6	0.4	14.4	0.6
40	13.3	1.7	14.6	0.4	14.4	0.6	14.3	0.7	14.0	1.0
60	13.1	1.9	14.4	0.6	14.2	0.8	14.0	1.0	13.5	1.5
80	12.7	2.3	14.2	0.8	14.0	1.0	13.7	1.3	13.3	1.7
100	12.6	2.4	14.0	1.0	13.7	1.3	13.4	1.6	13.1	1.9
120	12.3	2.7	13.8	1.2	13.5	1.5	13.2	1.8	12.9	2.1
140	12.0	3.0	13.5	1.5	13.0	2.0	12.7	2.3	12.5	2.5
160	11.6	3.4	13.0	2.0	12.7	2.3	12.1	2.9	11.9	3.1

Table 2. Summary of the rate (R) and the observed rate constant k_o of the inhibitory effect of halides ions

	None	KCl 0.1M	KCl 0.2M	KBr 0.1M	KBr 0.2M
$10^6 R$ mole/ l/sec	0.2219	0.1581	0.1594	0.2134	0.2365
$10^5 k_o$ sec^{-1}	2.64	1.66	1.75	1.99	2.61

The inhibitory effect of iodide ion could not be investigated because even at very low concentration of KI a reaction between KI and $K_2S_2O_8$ took place, in the case of KBr also a concentration equal to that of KCl could not be used as bromine was liberated due to the interaction of KBr with $K_2S_2O_8$, this leads to the conclusion that the specific inhibitory effect of Br ion is greater than that of Cl ion.

Comparing the curves in Figure (1) corresponding to the four different initial concentrations of halides indicate that the specific inhibitory effect of halides ions is in the order $F < Cl < Br < I$ and the specific inhibitory increased with increasing concentration. So we can conclude that the inhibitory effect of halides ions is not a proper salt effect and it is an instance of specific ionic effect, because when we used a very high concentration of potassium sulphate the decrease in the rate constant is much less than in the case of any halide ion.

Tables (3) and (4) show the influence of the mineral salt potassium sulphate on the thermal decomposition of 0.01 mole/l potassium peroxydisulphate at 70 °C. Results were represented graphically in Figure (2).

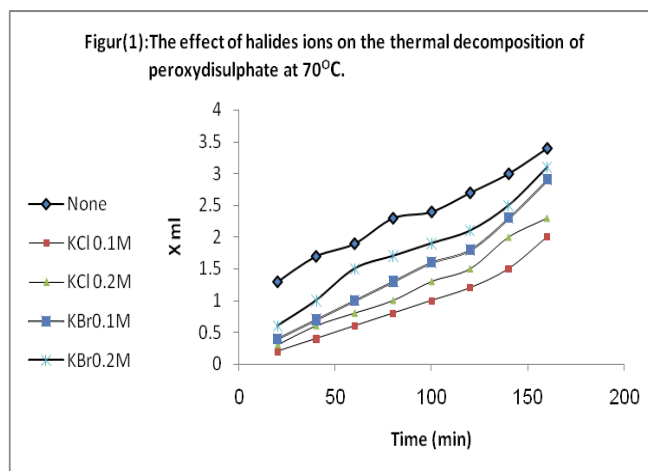


Figure 1. The effect of halides ions on the thermal decomposition of peroxydisulphate at 70 °C

Table 3. The influence of the mineral salt potassium sulphate on the thermal decomposition of potassium peroxydisulphate at 70 °C

Time min	None X ml	K ₂ SO ₄ 0.01M X ml	K ₂ SO ₄ 0.03M X ml	K ₂ SO ₄ 0.05M X ml
0	15.0	15.0	15.0	15.0
20	14.8	14.0	13.3	12.9
40	14.1	13.4	12.8	12.1
60	13.7	12.7	12.2	11.6
80	13.3	12.5	11.8	11.1
100	12.9	12.1	11.2	10.2
120	12.5	11.9	10.7	9.2
140	12.3	11.7	10.0	9.0
160	12.0	11.5	9.7	8.9

Table 4. Summary of the rate (R) and the observed rate constant k_0 due to the influence of the mineral salt potassium sulphate on the thermal decomposition of potassium peroxydisulphate at 70 °C

	None	K ₂ SO ₄ 0.01M	K ₂ SO ₄ 0.03M	K ₂ SO ₄ 0.05M
$10^6 R$ mole/ l/sec	0.2219	0.4240	0.3677	0.2427
$10^5 k_0$ sec ⁻¹	2.64	5.60	4.75	4.14

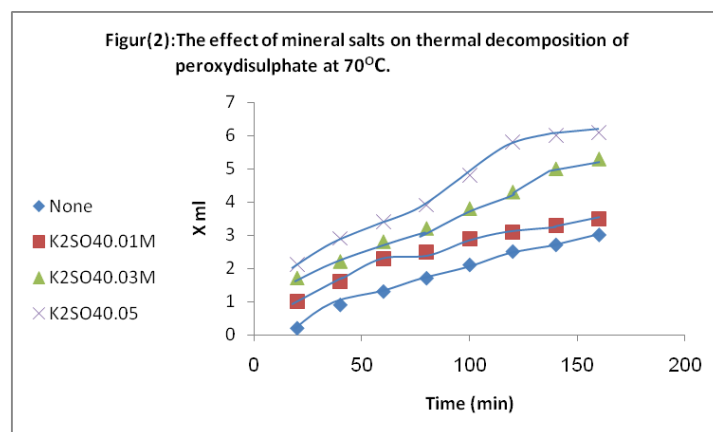


Figure 2. The effect of mineral salts on the thermal decomposition of peroxydisulphate at 70 °C

Tables (5) and (6) show the effect of the electrolytes, hydrochloric acid, potassium chloride, sulphuric acid and potassium sulphate and the non-electrolyte urea on the thermal decomposition of potassium peroxydisulphate at 70 °C in which its concentration was kept constant at **0.01** mole/l . Results were represented graphically in Figure (3).

Table 5. The effect of electrolytes and non-electrolyte on the thermal decomposition of potassium peroxydisulphate at 70 °C

Time min	H ₂ SO ₄ 0.05M	X ml	KCl 0.05M	X ml	K ₂ SO ₄ 0.05M	X ml	Urea 0.05M	X ml	HCl 0.05M	X ml
0	15.0		15.0		15.0		15.0		15.0	
20	14.6	0.4	14.2	0.8	14.8	0.2	14.8	0.2	13.9	1.1
40	14.1	0.9	14.7	1.3	14.6	0.4	14.7	0.3	13.3	1.7
60	13.8	1.2	13.3	1.7	14.4	0.6	14.5	0.5	12.9	2.1
80	13.2	1.8	12.8	2.2	14.1	0.9	14.3	0.7	12.3	2.7
100	12.8	2.2	12.4	2.6	13.7	1.3	14.1	0.9	12.0	3
120	12.3	2.7	11.8	3.2	13.0	2	13.6	1.4	11.5	3.5
140	12.0	3	11.4	3.6	12.8	2.2	13.2	1.8	11.1	3.9
160	11.3	3.7	10.9	4.1	12.2	2.8	12.7	2.3	10.5	4.5

Table 6. Summary of the rate (R) and the observed rate constant k_0 of the effect of electrolytes and non-electrolytes

	None	HCl 0.05M	KCl 0.05M	H ₂ SO ₄ 0.05M	K ₂ SO ₄ 0.05M	Urea 0.05M
$10^6 R$ mole/ l/sec	0.2219	0.2885	0.2844	0.2636	0.2154	0.1746
$10^5 k_0$ sec ⁻¹	2.64	3.30	2.80	2.75	1.99	1.40

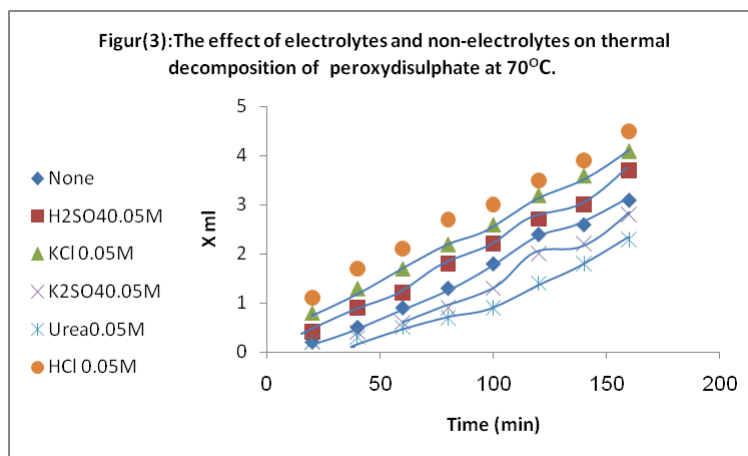


Figure 3. The effect of electrolytes and non-electrolytes on the thermal decomposition of peroxydisulphate at 70 °C

Tables (7) and (8) show the influence of mercuric chloride on the thermal decomposition of 0.01 mole/l potassium peroxydisulphate at 70 °C. Results were represented graphically in Figure (4).

Table 7. The influence of mercuric chloride on the thermal decomposition of potassium peroxydisulphate at 70 °C

Time min	None	X ml	HgCl ₂ 0.002M	X ml	HgCl ₂ 0.005M	X ml	HgCl ₂ 0.01M	X ml
0	15.0		15.0		15.0		15.0	
20	13.8	1.2	14.2	0.8	14.5	0.5	13.2	1.8
40	13.3	1.7	13.9	1.1	14.2	0.8	12.9	2.1
60	13.0	2	13.4	1.6	13.8	1.2	12.5	2.5
80	12.7	2.3	13.1	1.9	13.5	1.5	12.2	2.8
100	12.5	2.5	12.9	2.1	13.2	1.8	12.0	3
120	12.1	2.9	12.5	2.5	12.8	2.2	11.7	3.3
140	11.6	3.4	12.0	3	12.4	2.6	11.3	3.7
160	11.0	4	11.3	3.7	11.9	3.1	10.6	4.4

Table 8. Summary of the rate (R) and the observed rate constant k_o due to the influence of mercuric chloride on the thermal decomposition of potassium peroxydisulphate at 70 °C

	None	HgCl ₂ 0.002M	HgCl ₂ 0.005M	HgCl ₂ 0.01M
$10^6 R$ mole/ l/sec	0.2219	0.2573	0.2572	0.3469
$10^5 k_o$ sec ⁻¹	2.64	2.68	2.83	4.19

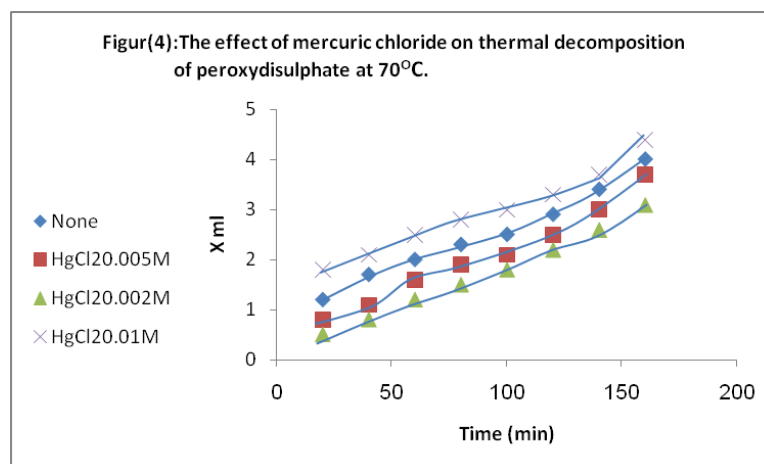


Figure 4. The effect of mercuric chloride on the thermal decomposition of peroxydisulphate at 70 °C

4. Conclusions

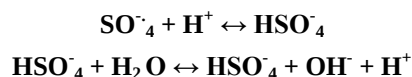
Comparing the curves in Figure (1) corresponding to the four different initial concentrations of halides indicate that the specific inhibitory effect of halides ions is in the order $F < Cl < Br < I$ and the specific inhibitory increased with increasing concentration. So we can conclude that the inhibitory effect of halides ions is not a proper salt effect and it is an instance of specific ionic effect, because when we used a very high concentration of potassium sulphate the decrease in the rate constant is much less than in the case of any halide ion.

It is obvious from Tables (3) and (4) that in the presence of potassium sulphate, the value of the rate constant k_0 first decreases with time i.e. the salt effect is negative, reaches a minimum and then increases again which indicates that the reaction becomes auto-catalytic in the later stages. This behavior can be explained on the assumption that potassium sulphate acts as an inhibitor, so the auto-catalytic nature of the reaction does not appear in the initial stages because K_2SO_4 is formed in the reaction mixture, but after some time when it is decomposed by potassium peroxydisulphate, the reaction again becomes auto-catalytic.

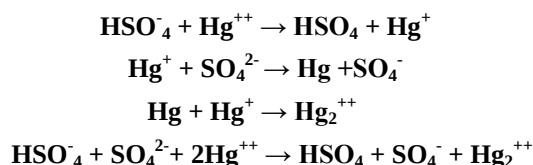
From Table (6), Figure (3) it is obvious that electrolytes and non-electrolytes have a catalyzing influence on the thermal decomposition of potassium peroxydisulphate in the following order



The catalyzing influence of HCl and H_2SO_4 may be mainly due to the H^+ ion, which may catalyze the reaction by the following steps:



Tables (7) and (8) show the catalytic influence of mercuric chloride on the thermal decomposition of peroxydisulphate and it may be due to the production of other chain carriers as a result of the interaction between HSO_4^- and Hg ion, which may bring about the thermal decomposition of peroxydisulphate as shown by the following steps (Vasudeva, 1969):



This requires the reduction of mercuric chloride to mercurous chloride, and this has actually been observed that as the concentration of Hg^{++} ions increase, the catalytic influence increases.

References

- Bartlett, P. D., & Cotman, J. D. (1949). *J. Amer. Chem. Soc.*, 71, 1419.
- Fronaeus, S., & Ostman, C. O., (1955). The Kinetics and Mechanism of the Reaction between Cerium(III) and Persulphate. *Acta. Chem. Scand.*, 9, 902. <http://dx.doi.org/10.3891/acta.chem.scand.09-0902>

- Green, L., & Mason, D. O. (1910). CCXIX.—The dynamics of the decomposition of persulphuric acid and its salts in aqueous solution. *J. Chem. Soc.*, 97, 2083. <http://dx.doi.org/10.1039/ct9109702083>
- Kolthoff, I. M, & Miller, I. K., (1951). The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium. *J. Amer.Chem. Soc*, 73, 3055. <http://dx.doi.org/10.1021/ja01151a024>
- Levi, M. G, Migliorini, E., & Gazz, A. (1963). *Chim Ltal.*, 36(ii), 599.
- Levitt, L.S, (1953). A New Mechanism For Persulphate Oxidations. *Canad. J. Chem*, 31, 915. <http://dx.doi.org/10.1139/v53-122>
- Morgan, J. L., & Christ, R. H., (1927). The Photochemical Decomposition Of Potassium Persulfate II. *J. Amer. Chem. Soc.*, 49, 338-961. <http://dx.doi.org/10.1021/ja01401a004>
- Rosin, J. (1946). *Reagents Chemicals and standards* (2nd ed.). New. York: D. van Nostrand. CO. Inc. p. 349.
- Vasudeva, W. C. (1969). Ph. D thesis, Fac. of Science, U. Of K.