

Evaluation of Thermodynamic Properties and the effect of surface on the Uncatalyzed Thermal Decomposition of Potassium Peroxydisulphate in Neutral Solution

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Abstract

The uncatalyzed thermal decomposition of potassium peroxydisulphate in neutral solution was studied titrimetrically. The progress of the reaction was followed by examining the concentration of persulphate ion in the reaction mixture at different time intervals by iodometric titration method. The study showed that the decomposition follows a first order kinetics and the reaction has a characteristic of chain reactions.

Thermodynamic properties namely activation energy (ΔE_a), frequency factor (A), entropy change (ΔS) and the free energy change (ΔG) of the uncatalyzed thermal decomposition were evaluated from the values of the fractional order rate constants k_0 at different temperatures. The effect of surface on the uncatalyzed thermal decomposition of persulphate ion alone was also investigated by carrying a set of experiments.

Keywords: Thermodynamic Properties, Thermal Decomposition, Effect of surface.

Introduction

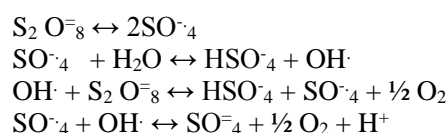
The thermal decomposition of potassium peroxydisulphate was the subject of study of many workers.¹⁻³ Earlier workers⁴ studying the thermal decomposition of potassium peroxydisulphate found that the decomposition in aqueous solution was accelerated by rise of temperature and depends on the concentration of solution.

Levr and Migliorini⁵ have found that the thermal decomposition of potassium peroxydisulphate was unimolecular and is catalyzed by acid and they observed that peroxydisulphate solutions which were stable at 35°C decompose catalytically by the hydrogen and the hydroxyl ions as well as platinum black and lead.

Bartlett and Cottman⁶ have suggested that the radicals produced in the peroxydisulphate ion decomposition in aqueous solution cannot induce the decomposition of the ion, so autocatalysis is not observed in the thermal decomposition of peroxydisulphate.

Fronaeus and Ostman⁷ and Kolthoff and Miller⁸ showed that the rate constant of the decomposition was independent of the ionic strength but in acid solution there is a negative salt

effect. Abualreish and Aissa⁹ 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 Cottman⁶ suggested for the uncatalyzed thermal decomposition the following chain mechanism:



Another mechanism for the uncatalyzed thermal decomposition was suggested by Fronaeus and Ostman⁷ and Levitt¹⁰. All the workers studying the uncatalysed thermal decomposition of potassium peroxydisulphate suggested the following rate law.

$$R = \frac{-d[S_2O_8^{2-}]}{dt} = k_0[S_2O_8^{2-}]$$

where R is the rate of the reaction evaluated by the relation:

$$R = \frac{\Delta m}{\Delta t} \text{ mole/L/second}$$

$$\Delta m = m - m'' \quad \text{mole/L}$$

Δt is the difference in time.

k_0 is the observed rate constant which can be estimated by the integrated rate law for a first order reaction as follows:

$$k_0 = \frac{2.303}{t} \log \frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]}$$

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 Cotman⁶ and Rosin.¹¹ The kinetic measurements were carried out over the temperature range of 60 - 80°C.

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 by the equation:

$$\begin{aligned} E_a &= - \text{slope} \times 2.303 \times R \text{ cal/mole} \\ R &= 1.987 \text{ cal/mole} \end{aligned}$$

or = 8.314 J/mole.

The value of the frequency factor A (in sec^{-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:

$$\Delta S = 2.303R (\log A - \log RT/Nh) \text{ J/K}^\circ$$

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

$$\Delta G = \Delta E_a - T\Delta S \text{ KJ/mole.}$$

Experimental

All chemicals used were of 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 range of temperature 60- 80°C was used.

Results and Discussion

Evaluation of Thermodynamic Properties: Table 1 includes the result of the kinetic run of the uncatalysed thermal decomposition of potassium peroxydisulphate at a temperature of 60°C (container used a 250 ml round bottom flask and glass stoppered) in which the initial concentration of peroxydisulphate (m) at zero time of decomposition was varied from 0.005 to 0.1 mole/l while (m'') represents the mean concentration at time t of decomposition of the same kinetic run.

Figure (1) represents the plot of the rate R of the uncatalysed thermal decomposition of potassium peroxydisulphate in mole/l/sec against the peroxydisulphate mean concentration (m'') in mole/l which is linear and satisfies the relationship:

$$R = \frac{-d[S_2O_8^{2-}]}{dt} = k_0[S_2O_8^{2-}]$$

Table 1

The initial concentration of peroxydisulphate (m), peroxydisulphate mean concentration (m''), rate (R) and rate constant (k₀) data of the thermal decomposition of potassium peroxydisulphate at 60 °C

(m) [S ₂ O ₈ ⁼] ₀ mole/l	(m'') [S ₂ O ₈ ⁼] _{Aver} mole/l	10 ⁶ R mole l ⁻¹ sec ⁻¹	10 ⁵ k ₀ sec ⁻¹
0.005	0.0037857	0.023498	0.66
0.01	0.0079964	0.041178	0.56
0.02	0.016999	0.1718403	1.09
0.04	0.032932	0.2023816	0.61
0.06	0.047432	0.279064	0.58
0.08	0.064146	0.356048	0.51
0.1	0.084107	0.4309271	0.52

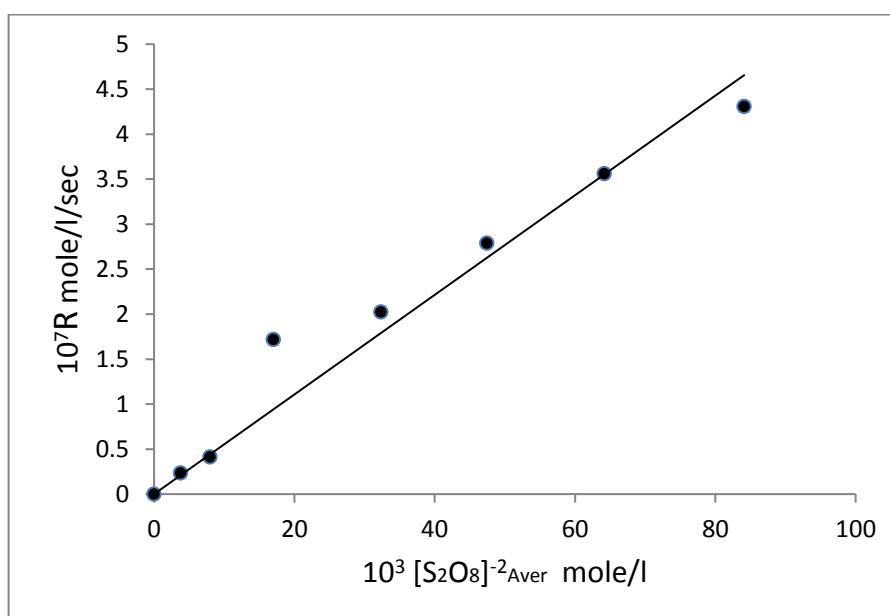


Figure 1: Plot of the rate R against $[S_2O_8]^{2-}$ Aver for the uncatalysed thermal decomposition of peroxydisulphate at 60°C

Figure 2 represents the plot of the rate R of the uncatalysed thermal decomposition of potassium peroxydisulphate in mole/l/sec against the initial concentration of peroxydisulphate (m) in mole/l which is also linear and satisfies the relation:

$$R = K_0 [S_2O_8^{2-}]_0$$

The above equation shows that the uncatalysed thermal decomposition of potassium peroxydisulphate is of first order in peroxydisulphate concentration.

The slope of figure 1 has a value equal to k_0 or $0.54 \times 10^{-5} \text{ sec}^{-1}$, the value is confirmed from the plot of the values of k_0 from table 1 against the initial concentration of peroxydisulphate (m) which is linear and parallel to the concentration axis giving a graphical mean of $0.53 \times 10^{-5} \text{ sec}^{-1}$ (figure 3).

Tables 2 to 5 include the results of the experiments carried out at a constant peroxydisulphate concentration of 0.02 mole/l and over the temperature range 60, 70, 75 and 80°C.

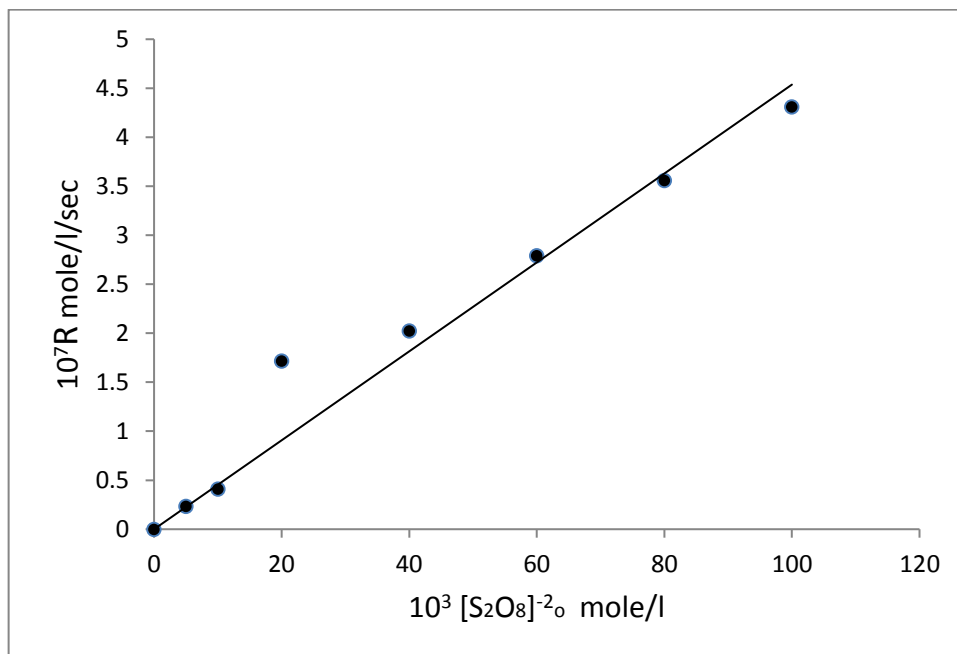


Figure 2: Plot of the rate R against $[S_2O_8]^{2-}_0$ for the uncatalysed thermal decomposition of peroxydisulphate at 60°C

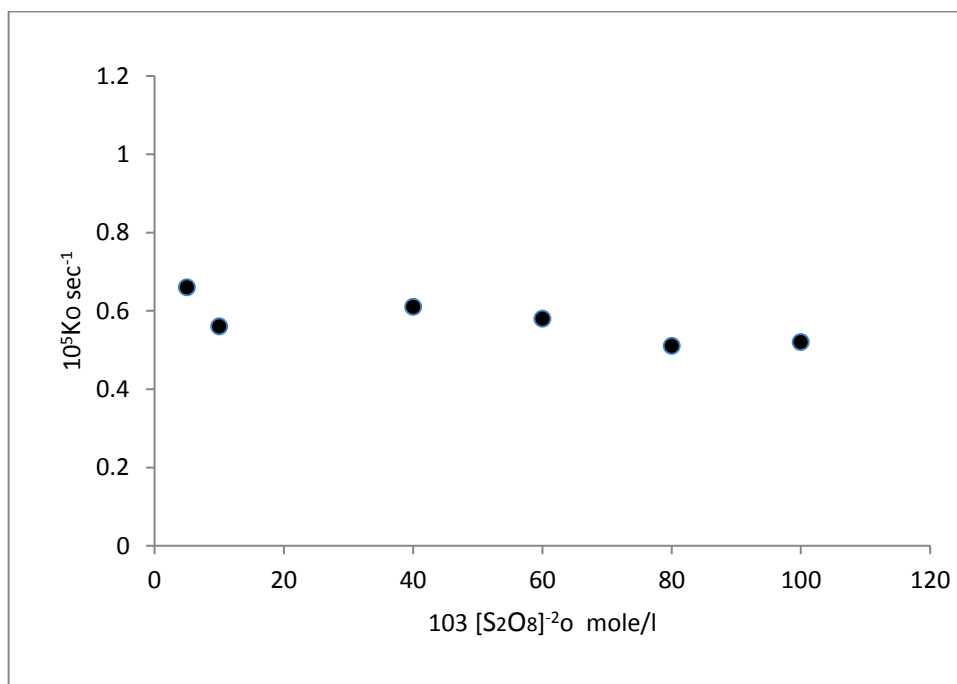


Figure 3: Plot of the rate constant K_0 against $[S_2O_8]^{2-}_0$ for the uncatalysed thermal decomposition of peroxydisulphate at 60°C

Table 2

The rate constant K_0 for the uncatalysed thermal decomposition of peroxydisulphate at 60°C

Time sec	Titre ml	$10^5 k_0 \text{ sec}^{-1}$ at 60 °C
0	9.70	
3600	8.90	2.39*
7200	8.60	1.67*
10800	8.45	1.28
14400	8.25	1.12
18000	8.00	1.07
21600	7.70	1.07
15200	7.55	0.99
32400	7.05	0.98
Mean		1.09

Table 3

The rate constant K_0 for the uncatalysed thermal decomposition of peroxydisulphate at 70°C

Time sec	Titre ml	$10^5 k_0 \text{ sec}^{-1}$ at 70 °C
0	9.00	
3600	7.60	4.70*
6300	7.30	3.32
9000	6.95	2.87
11700	5.50	2.78
14400	6.10	2.70
Mean		2.92

Table 4

The rate constant K_0 for the uncatalysed thermal decomposition of peroxydisulphate at 75°C

Time sec	Titre ml	$10^5 k_0 \text{ sec}^{-1}$ at 75 °C
0	9.65	
1800	7.75	12.18*
3600	7.40	7.37
5400	6.60	7.03
7200	5.90	6.83
9000	5.60	6.05
Mean		6.82

Table 5

The rate constant K_0 for the uncatalysed thermal decomposition of peroxydisulphate at 80°C

Time sec	Titre ml	$10^5 k_0 \text{ sec}^{-1}$ at 80 °C
0	9.50	
900	8.25	15.68*
1800	7.25	15.02
2700	6.90	11.84
3600	5.20	11.85
4500	5.85	10.77
Mean		12.37

*The asterisk values are not included in the calculation of the mean of k_0

Table 6
Summary of tables 2-5

T K°	10 ³ 1/T	10 ⁵ k _o sec ⁻¹	5+log k _o
333	3.003	1.09	0.037426
343	2.915	2.92	0.465383
348	2.874	6.82	0.833784
353	2.833	12.37	1.09237

Table 7
Thermodynamic properties for the uncatalysed thermal decomposition of potassium peroxydisulphate in neutral solution

Physical parameter	Found			
Activation Energy (E _a) in Kcal/mole	28.70			
Frequency factor (A) in sec ⁻¹	12.30X10 ⁻⁵			
Free energy change (ΔG) in Kcal/mole at different temperatures	60°	70°	75°	80°
	10.78	10.22	9.94	9.66
Entropy change (ΔS) in cal/K°at different temperatures	60°	70°	75°	80°
	-53.83	-53.89	-53.91	-53.94

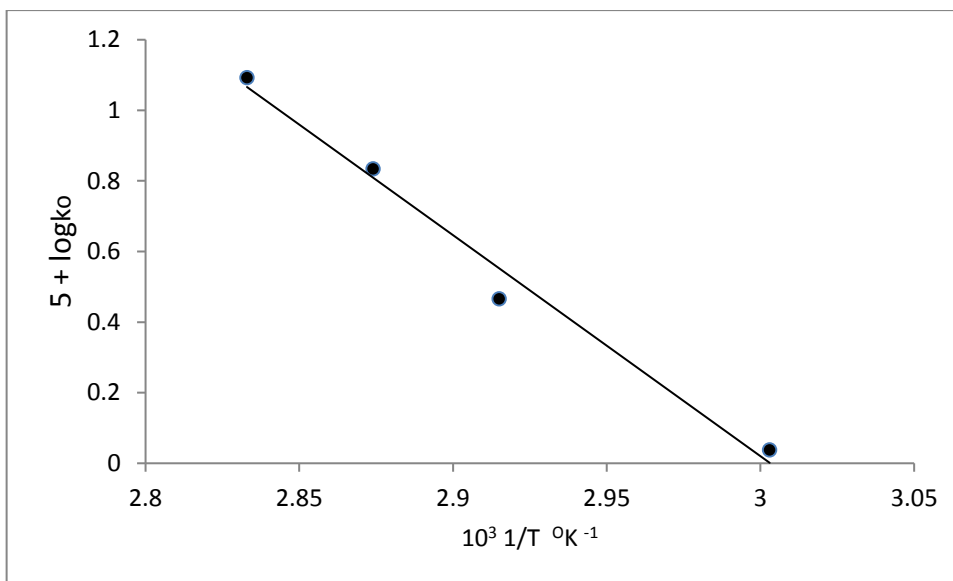


Figure 4: Activation energy for the uncatalysed thermal decomposition of peroxydisulphate

The plot of $\log k_o$ against $1/T$ gave straight line and from the slope of the line, the energy of activation (E_a) for the uncatalysed thermal decomposition of peroxydisulphate was calculated and also the frequency factor (A) from the intercept of the line. Moreover, the entropy change (ΔS) and the free energy change (ΔG) at specific temperature were also calculated. Results are summarized in table 7.

The effect of surface: To investigate the effect of increasing the surface area of the reaction vessel on the uncatalysed thermal decomposition potassium peroxydisulphate in neutral solution, a set of experiments were carried out in which the surface employed consisted mostly of small pieces of porcelain, silica, pyrex glass and glass wool. The results of these experiments are summarized in table 8. The

data in table 8 indicate the great sensitivity of this reaction to added surface as the rate of decomposition of potassium peroxydisulphate increased between 20-60%. This fact confirms the chain character of the uncatalysed thermal decomposition of potassium peroxydisulphate in the absence of substrate.¹²

Table 9 includes the result of the kinetic run of the uncatalysed thermal decomposition of potassium peroxydisulphate at a temperature of 60°C in which the initial concentration of peroxydisulphate (m) at zero time of decomposition was varied from 0.01 to 0.1 mole/l. The change of size of the reaction vessel affected the rate and the rate constant of the uncatalysed thermal decomposition of potassium peroxydisulphate in neutral solution as noticed from table 1 and table 9 by approximately 25-30 %.

Table 8

Effect of added surface on the uncatalysed thermal decomposition of potassium peroxydisulphate in neutral solution at constant potassium peroxydisulphate concentration of 0.02 mole/l and at 60°C

Surface	Weight in grams	% Decomposition of potassium peroxydisulphate in 300min
---	---	13.9
Pyrex glass pieces	20	17.9
Porcelain pieces	20	19.6
Silica pieces	20	16.8
Glass wool	20	22.3

Table 9

The result of the kinetic run of the uncatalysed thermal decomposition of potassium peroxydisulphate at a temperature of 60°C

(m) [S ₂ O ₈ ⁼] _o mole/l	(m'') [S ₂ O ₈ ⁼] _{Aver} mole/l	10 ⁶ R mole l ⁻¹ sec ⁻¹	10 ⁵ k _o sec ⁻¹
0.01	0.00943	0.0680	0.77
0.02	0.01790	0.1397	0.82
0.04	0.03718	0.2618	0.74
0.1	0.09203	0.651	0.71

The uncatalysed thermal decomposition of peroxydisulphate in neutral solutions shows a gradual increase in acidity which supports the stoichiometric equation:



Because of the great abundance of water in the system, its concentration may be regarded to remain constant and the decomposition of peroxydisulphate may be considered as a pseudounimolecular reaction obeying a first order rate law. The data in table 7 shows that the above reaction requires high activation energy (28.7 Kcal). This high value suggests that the peroxydisulphate ion consists of two sulphate groups which on activation break into two symmetrical sulphate radicals (SO₄[•]).

Conclusion

It is seen that from tables 2 to 5 the rate constants are in general higher in the initial part of the reaction, this observation was also noted for reactions of peroxydisulphate with the substrates¹³. This higher rate constant in the initial stages of the reaction can be due to the catalysing role which the surface of the reaction vessel plays between peroxydisulphate and hydroxyl radical.

With the progress of the reaction the concentration of the products (O₂ and HSO₄⁻ in this case) becomes appreciable and if these products occupy a part of the surface by adsorption, this will reduce the catalysing effect of the surface. After a while from the start of the reaction, a state of equilibrium prevails between product adsorption and surface catalysis and the observed rate constant (k_o) tends to be constant.

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