

Kinetics and Mechanisms of Oxidation of Thiosulphate Ion by Peroxodisulphate

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Abstract: The kinetics of the oxidation of thiosulphate ion $S_2O_3^{2-}$ by peroxodisulphate ion $S_2O_8^{2-}$ been studied out in system of high ionic strength and phosphate medium at 40°C. Under controlled conditions of ionic strength around one ($I \approx 1$) and constant cation concentration the reaction is of overall second order, being first order with respect to each peroxodisulphate and thiosulphate ions. The reaction takes place according to the stoichiometry $S_2O_8^{2-} + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + S_4O_6^{2-}$ and the rate law: $R_0 = k_1[S_2O_8^{2-}]_0 + k_2^0[S_2O_8^{2-}]_0[S_2O_3^{2-}]_0 + \{\sum k_{Mi^+}[M^+]\}[S_2O_8^{2-}]_0[S_2O_3^{2-}]_0$ Cations catalyze the reaction rate in the ascending order ($Li^+ < Na^+ < K^+$) and the extent of catalysis depends on the nature and concentration of the cations. The activation parameters have been evaluated and discussed and the mechanism has been proposed for the reaction.

Keywords: Peroxodisulphate; Thiosulphate(VI); Oxidation; Kinetics; Mechanism

1. Introduction

Peroxodisulphate ion $S_2O_8^{2-}$ are the most chemically active of the peroxygens, with great utility in a variety of chemical processes. Also Peroxodisulphate is one of the strongest oxidizing agents known in aqueous solution⁽¹⁾. Peroxodisulphuric acid and its salts were suggested to be among the most useful oxidizing agents in aqueous solution⁽²⁾ for variety of organic and inorganic compounds. Reactions involving peroxodisulphate ion are generally slow at ordinary temperatures⁽³⁾ but become more rapid in the presence of some metal ions like Ag(I), Fe(II) and Cu(II). Therefore in this work we used Na^+ and K^+ in the redox reaction between Peroxodisulphate ion and thiosulphate ion.

The kinetics study of the reaction of thiosulphate ion has been of increasing interest due to its biological and chemical implications⁽⁴⁾. It is used to dechlorinate tap water including lowering chlorine levels for use in aquaria and swimming pools. Thiosulphate ion is most effective in a pre-hospital setting, since immediate administration by emergency personnel is necessary to reverse rapid intracellular hypoxia caused by the inhibition of cellular respiration^(5,6).

2. Experimental

Materials

All employed chemicals in the present work were high purity (98%) and bidistilled water was used in the preparation of their solutions. The redox reaction of peroxodisulphate with thiosulphate ion proceeds at measurable rate at about 40°C and it is for this reason, that the temperature range 35⁰- 50⁰C was chosen. For each run two solutions A and B were prepared. A was freshly prepared $-K_2S_2O_8-$ while B was a mixture of $S_2O_3^{2-}$, added salts ($NaNO_3$ and KNO_3) which maintained the constant

ionic strength and phosphate buffer ($Na_2HKPO_4 - KH_2PO_4$). Solutions A and B were made in such way that the concentration of each species was double the value required in the final reaction mixture. Water carefully redistilled from alkaline $KMnO_4$ was used.

Preparation of Solutions

Solution A: Calculated amount of A.R $K_2S_2O_8$ was dissolved in double distilled water to make 500cm³ of solution A. Solution B: Calculated amount of $Na_2S_2O_3$, $NaNO_3$, KNO_3 and Phosphate buffer ($Na_2HPO_4 - KH_2PO_4$) are dissolved in double distilled water to make 500cm³ of solution B. Solutions of iodine, potassium dichromate and starch were freshly prepared.

Reaction Conditions

The redox reaction was carried out in the conditions: $[S_2O_8^{2-}]_0 = [S_2O_3^{2-}]_0$, high ionic strength around one ($I=0.80-1.34$), Phosphate buffer $[Na_2HPO_4]=[KH_2PO_4]=0.20 \text{ mol dm}^{-3}$.

Kinetics measurements:

The progress of the reaction was followed by determining the concentration of thiosulphate ion at various time interval. The mixture contained $S_2O_3^{2-}$ was titrated against standard solution of iodine.

3. Results & Discussion

Kinetic order with respect to Peroxodisulphate ion

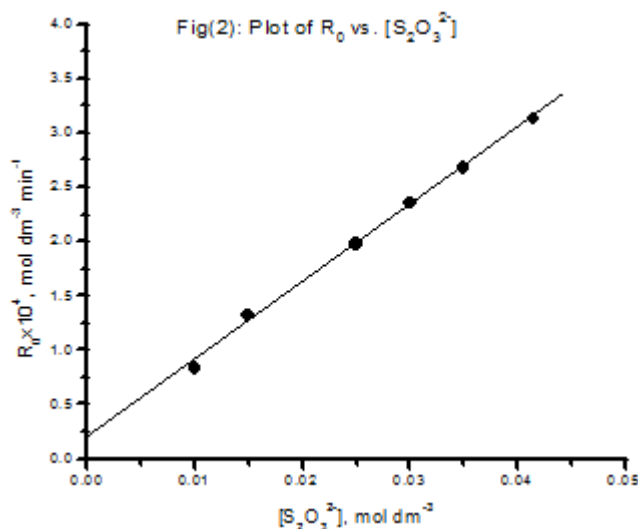
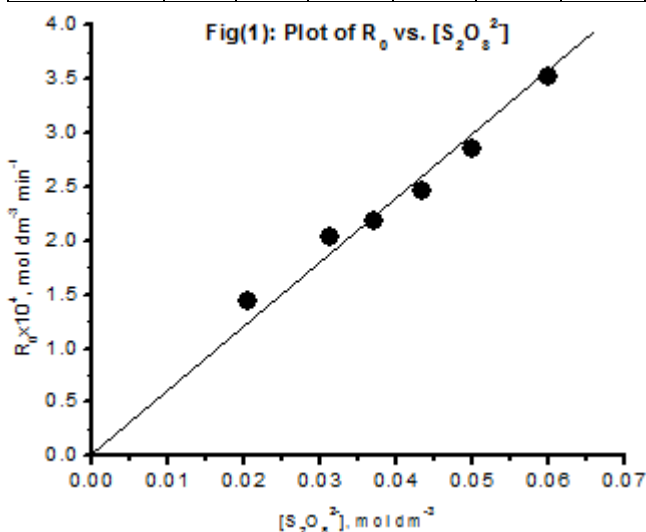
The effect of $S_2O_8^{2-}$ concentration on the rate of disappearance of thiosulphate ion was investigated under the constant conditions given in the captions of table (1). For each kinetic run the mean initial rates (R_0) are summeraze in table (1). A plot of R_0 vs. $[S_2O_8^{2-}]_0$ (fig.1) gives a straight line passing through the origin indicating that the reaction is first order with respect to $S_2O_8^{2-}$, thus:

$$R_0 = -d[S_2O_8^{2-}]_0/dt = k_{obs} [S_2O_8^{2-}]_0 \quad (1)$$

Where k_{obs} is initial-pseudo first order rate constant. From fig(1) the slope = $k_{obs} = 7.74 \times 10^{-3} \text{ min}^{-1}$, at 40°C .

Table 1: Variation of R_0 with $[S_2O_8^{2-}]_0$
 $[S_2O_3^{2-}]_0 = 0.0250 \text{ mol dm}^{-3}$
 $[Na^+] = [K^+] = 0.500 \text{ mol dm}^{-3}$
 $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$
 $I = 1.25 - 1.29$
 $pH = 6.85$
 $Temp. = 40^\circ\text{C}$

$[S_2O_8^{2-}]_0 / \text{mol dm}^{-3}$	0.0205	0.0313	0.0370	0.0435	0.0500	0.0600
$10^4 \times R_0, \text{mol dm}^{-3} \text{ min}^{-1}$	1.44	2.04	2.19	2.46	2.85	3.53



Effect of hydrogen ion

The effect of pH on the redox reaction was studied under the condition given in table (3) by changing the ratio $[HPO_4^{2-}]/[H_2PO_4^-]$. The pH was measured directly using a pH-meter. From table (3.3) there is no clear effect on R_0 . Hence it may be concluded that the rate of the reaction is independent of pH.

Table 3: Variation of R_0 with pH

$[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$ $[S_2O_3^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[Na^+] = [K^+] = 0.500 \text{ mol dm}^{-3}$ $I = 0.85 - 1.56$ $Temp. = 40^\circ\text{C}$

pH	03.86	04.38	06.36	06.52	07.46	08.15
$R \times 10^4, \text{mol dm}^{-3} \text{ min}^{-1}$	02.64	02.56	02.70	02.67	02.72	02.68

Kinetic order with respect to thiosulphate ion

The order with respect to initial concentration of thiosulphate ion was investigated under the constant conditions given in the caption of table (2). A plot of initial rate R_0 , of the disappearance of thiosulphate ion against the respective $[S_2O_3^{2-}]_0$ values, (fig.2) gives a straight line intercepting the y-axis at $R_1 = 3.607 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}$, having a slope of $C = 7.7419 \times 10^{-3} \text{ min}^{-1}$.

Thus the rate may be represented by the equation:

$$R_0 = -d[S_2O_3^{2-}]_0/dt = R_1 + C[S_2O_3^{2-}]_0 \quad (2)$$

The first term right hand side (r.h.s) R_1 represents the thermal decomposition of peroxodisulphate in the absence of thiosulphate ion while the second term represents the redox ($S_2O_8^{2-} - S_2O_3^{2-}$) path. Since the reaction is first order in $S_2O_3^{2-}$ equation (3) can be rewritten as:

$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (3)$$

Where k_1 is the thermal decomposition of peroxodisulphate and k_2 is second order rate constant.

Table 2: Variation of R_0 with $[S_2O_3^{2-}]_0$
 $[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$ $[Na^+] = [K^+] = 0.500 \text{ mol dm}^{-3}$
 $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$ $I = 1.09 - 1.15$
 $pH = 6.47$ $Temp. = 60^\circ\text{C}$

$[S_2O_3^{2-}]_0 / \text{mol dm}^{-3}$	0.0100	0.0150	0.0250	0.0300	0.0350	0.0415
$10^4 \times R_0 / \text{mol dm}^{-3} \text{ min}^{-1}$	0.8357	1.3200	1.9800	2.3500	2.6700	3.1300

Free radical scavengers effect

The effect of adding allylacetate as a free radical scavenger in concentrations range $6.53 \times 10^{-3} \text{ mol dm}^{-3}$ to $14.54 \times 10^{-3} \text{ mol dm}^{-3}$ was investigated by carrying out the runs in experimental conditions given in the caption of table (4). No clear effect of addition of allylacetate was observed. Thus free radicals scavenger are not involved in the rate law.

Table 4: Variation of R_0 with Allyl acetate

$[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$ $[S_2O_3^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[Na^+] = [K^+] = 0.500 \text{ mol dm}^{-3}$
 $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$
 $I = 1.27$ $pH = 6.85$ $Temp. = 40^\circ\text{C}$

$10^3 [Allyl \text{ acetate}] / \text{mol dm}^{-3}$	Nil	06.53	08.63	10.53	12.54	14.64
$10^5 \times R_0 / \text{mol dm}^{-3} \text{ min}^{-1}$	02.68	02.74	02.69	02.66	02.65	02.62

Effect of added salts

The effect of added salts Li_2SO_4 , $NaNO_3$, Na_2SO_4 and KNO_3 on the redox reaction was studied by changing the concentrations of salts to study the effect of cations (Li^+ , Na^+ and K^+) and anions NO_3^- and SO_4^{2-} . Under otherwise constant experimental conditions given in tables (5). It is clear from (figs.3 and 4) that the rate of the reaction is linearly to cations concentrations. Moreover, (fig.3) (straight line -B- and table(6 and 7) confirmed that the effect is due to the cation and not to the anion. thus the rate of the reaction may be expressed by equation(4):-

$$R_0 = C + k_{obs} [M^{+n}] \quad (4)$$

In which C is y-intercept at $[M^+] = 0$ and k_{obs} is slope of the straight lines, as defined by the equations (5) and (6) respectively:

$$C = k_1[S_2O_8^{2-}]_0 + k_2^0[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 + k_{Mi}^+[M_i^+][S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (5)$$

$$k_{obs} = k_M^+ [S_2O_8^{2-}] [S_2O_3^{2-}] \quad (6)$$

where k_M^+ is the catalytic rate constant for the cation M^+ under study, k_{Mi}^+ is that of the residual cation M^+ and k_2^0 is the second order rate constant at zero cation concentration. Substituting the relevant values of C and k_{obs} from each plot and the appropriate values of the other terms applicable to it leads to the results given in tables (5 and 6). Thus it is evident that the cations catalyze the redox reaction and that they do so in the ascending order $Li^+ < Na^+ < K^+$.

Table 5: Effect of added salts

$[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[S_2O_3^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$
 $I = 1.01-1.75$
 $pH = 6.85$
 $Temp. = 40^\circ C$

KNO ₃		NaNO ₃		Na ₂ SO ₄		Li ₂ SO ₄	
[K ⁺] mol dm ⁻³	Rx10 ⁴ mol dm ⁻³ min ⁻¹	[Na ⁺] mol dm ⁻³	Rx10 ⁴ mol dm ⁻³ min ⁻¹	[Na ⁺] mol dm ⁻³	Rx10 ⁴ mol dm ⁻³ min ⁻¹	[Li ⁺] mol dm ⁻³	Rx10 ⁴ mol dm ⁻³ min ⁻¹
00.400	02.680	00.500	02.680	00.500	02.690	00.050	02.520
00.500	03.140	00.600	02.900	00.600	02.860	00.100	02.570
00.600	03.250	00.700	02.990	00.700	03.010	00.200	02.670
00.800	03.800	00.800	03.190	00.800	03.140	00.300	02.780
00.900	04.170	00.900	03.220	00.900	03.350	00.350	02.810
01.000	04.350	01.000	03.460	01.000	03.490	-----	-----

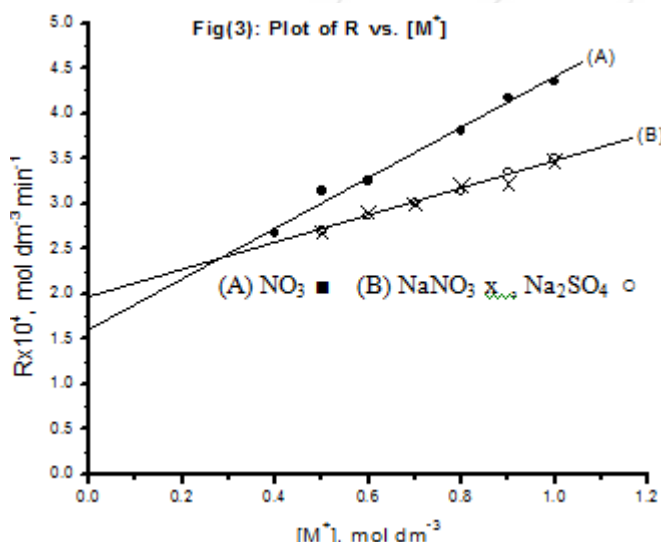


Table 6: Variation of Cation M^+ with k_{obs} and k_M^+

Cation	Cx10 ⁴ (intercept) mol dm ³ s ⁻¹	$k_{obs} \times 10^4 \text{ min}^{-1}$	$k_M^+ \times 10^2 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}$
Li ⁺	2.74	1.05±0.01	08.61±0.03
Na ⁺	1.98	1.57±0.03	12.82±0.01
K ⁺	1.65	2.70±0.04	22.26±0.02

The rate law for the reaction is thus detailed as in equation 7.
 $R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 + \{ \sum k_{Mi}^+[M_i^+] \} [S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (7)$

Where k_{Mi}^+ is the catalytic rate constant for i^{th} ion.

Where $i = 1$, represents the cations present in the system. When only one cation is present the term within the Σ sign reduces to $k_M^+[M^+]$ and equation becomes:

$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 + k_M^+[M^+] [S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (8)$$

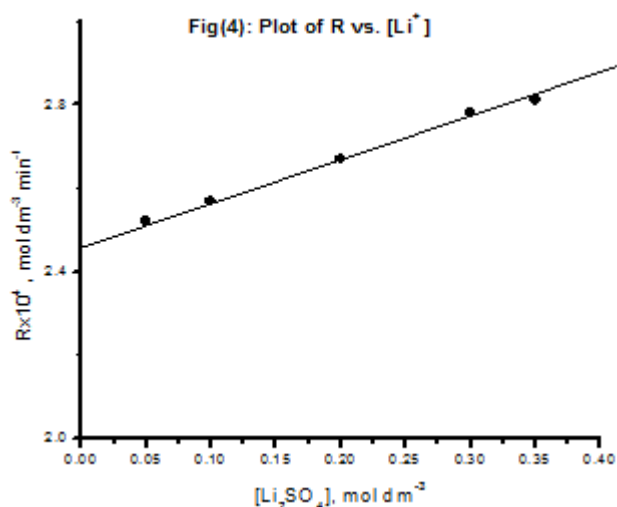


Table 7: Variation of NaNO₃ and Na₂SO₄ with k_M^+

$[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[S_2O_3^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$
 $[K^+]_{resid} = 0.4000 \text{ mol dm}^{-3}$
 $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$
 $I = 1.14-2.03$
 $pH = 6.85$
 $Temp. = 40^\circ C$

Salt	$k_{obs} \times 10^4 \text{ min}^{-1}$	$k_M^+ \times 10^2 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}$
NaNO ₃	1.621	13.24
Na ₂ SO ₄	1.570	12.82

Effect of temperature

The variation of the second order rate constant k_2 was studied over the temperature range 35-50°C at other wise constant experimental conditions of $[S_2O_8^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$, $[S_2O_3^{2-}]_0 = 0.0350 \text{ mol dm}^{-3}$, $[Na^+] = [K^+] = 0.500 \text{ mol dm}^{-3}$, $[HPO_4^{2-}] = [H_2PO_4^-] = 0.20 \text{ mol dm}^{-3}$, $I = 1.24$ and $pH = 6.85$. Table (8) summarise the results of four kinetic runs. The values of the first order

rate constant for the thermal decomposition of $S_2O_8^{2-}$, k_1 , were used in calculating k_2 at each temperature from equ.5. Results are summarised in table(8).

The effect of temperature on k_2 components (i.e. k_2^0 and k_M^+) was also studied in the range 35-50C⁰. For each temperature k_2 was calculated from equation 3, and then k_M^+ was calculated from y-intercept of (fig.5) resulting from plot of $[M^+]$ vs. R_0 by using the equation

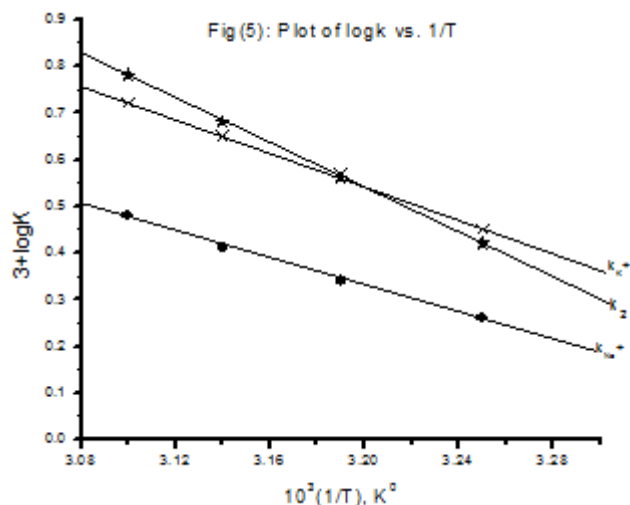
$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2^0[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 + k_M^+[M^+][S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (9)$$

From plot of $\log k_M^+$ against $1/T$ the relevant Arrhenius parameters were calculated in table (7) for each path.

Table 8: Thermodynamics parameters of activation

$$\begin{aligned} [S_2O_8^{2-}]_0 &= 0.0350 \text{ mol dm}^{-3} \\ [S_2O_3^{2-}]_0 &= 0.0350 \text{ mol dm}^{-3} \\ [Na^+] = [K^+] &= 0.500 \text{ mol dm}^{-3} \\ [HPO_4^{2-}] = [H_2PO_4^-] &= 0.20 \text{ mol dm}^{-3} \\ I &= 1.24 \\ pH &= 6.85 \end{aligned}$$

Temp. ⁰ C	35	40	45	50
$10^3 \times k_2, \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$	2.62	3.63	4.80	6.03
$10^4 \times k_{Na^+}, \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$	18.20	22.07	25.92	30.23
$10^4 \times k_{K^+}, \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$	28.18	36.77	44.22	52.47
Path	$\Delta E^\ddagger / \text{kJmol}^{-1}$	A	$\Delta S^\ddagger / \text{JK}^{-1}$	$\Delta G^\ddagger / \text{kJmol}^{-1}$
k_2	33.87	8.21×10^2	189.57	25.47
k_{Na^+}	29.05	2.61×10^3	199.00	33.24
k_{K^+}	46.31	19.49×10^3	143.98	12.41



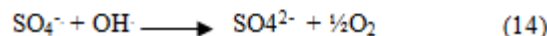
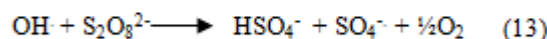
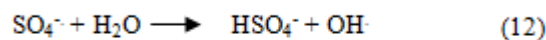
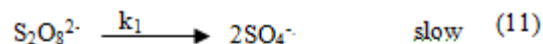
4. Discussion

A proposed mechanism

From equation (8) there are three paths of mechanism, each one from the term of the general rate law of the oxidation of thiosulphate ion by peroxodisulphate in presence of cations is:

1-Thermal decomposition of peroxodisulphate- k_1 - Path:

It is clear from first term $\{k_1[S_2O_8^{2-}]_0\}$ of equ.(8) is independent of substance $S_2O_3^{2-}$ ion which has its rate-determining step in equ.(11)



Some $SO_4^{\cdot-}$ radicals seem to end up forming oxygen according to well established mechanism discussed by House⁽⁷⁾, while most $SO_4^{\cdot-}$ radicals seem to oxidize $S_2O_3^{2-}$ ion in some faster steps represented by the overall equ.(15).



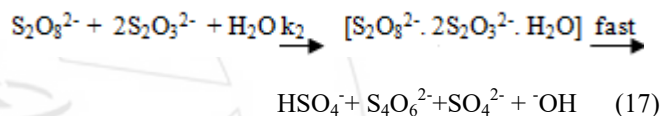
Therefore the rate equation of this path may represent by the equ.(16)

$$\text{Rate} = k_1 [S_2O_8^{2-}]_0 \quad (16)$$

Which corresponds to the first term of the r.h.s. of equation (8).

2- Observed second order rate constant- k_2 -Path:

In this path the rate determining step involves both $S_2O_8^{2-}$ and $S_2O_3^{2-}$ which in presence of water leads to products as:



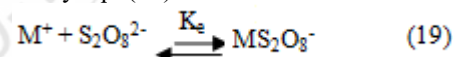
The rate equation is:

$$-d[S_2O_8^{2-}]_0/dt = k_2[S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (18)$$

And this explains the second term on the r.h.s. of equ.(8)

3- Catalytic rate constant- k_M^+ -Path:

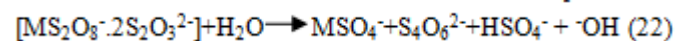
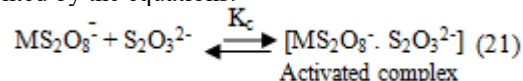
Because of the specific structure of $S_2O_8^{2-}$ forms an ion-pair faster than $S_2O_3^{2-}$ with the cations (Na^+ and K^+) in fast equilibrium represented by equ.(19):



Which gives

$$K_e = [MS_2O_8^-] / [M^+][S_2O_8^{2-}] \quad (20)$$

Thiosulphate ion is expected to react with the ion-pair faster than its reaction with the un-associated $S_2O_8^{2-}$ ion^(8,9) due to the decrease of coulombic barrier. The resulting activated complex formed by the interaction between $S_2O_3^{2-}$ and $MS_2O_8^-$ decomposes to form reaction products in a series of steps represented by the equations:



Equation (21) is the rate determining step and therefore the rate equation is:

$$\text{Rate} = k_c[MS_2O_8^-][S_2O_3^{2-}] \quad (23)$$

Substituting the value of $[MS_2O_8^-]$ obtained from rearranging equ.20 in equ.23 gives:-

$$\text{Rate} = K_e k_c [M^+][S_2O_8^{2-}][S_2O_3^{2-}] \quad (24)$$

This equation explain the catalytic effect of the cations (i.e. Na^+ and K^+).

Which can be reduces to:-

$$\text{Rate} = k_M^+[M^+][S_2O_8^{2-}][S_2O_3^{2-}] \quad (25)$$

This is equivalent to the third term of the r.h.s. of equation (8). When i is set equal to one and when:

$$k_M^+ = K_c k_c \quad (26)$$

Equation (8) can be rewritten as:

$$R_0 = k_1 [S_2O_8^{2-}]_0 + k_2^0 [S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 + K_c k_c [M^+] [S_2O_8^{2-}]_0 [S_2O_3^{2-}]_0 \quad (27)$$

Under the conditions of k_M^+ path the stability of the ion-pair $M^+, S_2O_8^{2-}$ is concerned to the size of M^+ and this decreases⁽¹⁰⁾ in order $K^+ > Na^+ > Li^+$. However, the catalytic effect of the cations must be increases in the order $Li^+ < Na^+ < K^+$.

5. Acknowledgement

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