CHAPTER-IV
OXIDATION OF CROTONAMIDE

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Preliminary experiments showed that the reaction of $S_2O_8^{2-}$ ion with crotonamide is extremely low at room temperature without any catalyst. The reaction proceeds with a measurable velocity at room temperature, provided that small amount of $(2.0 \times 10^{-3}M)$ $AgNO_3$ was used as a catalyst in the reaction mixture. Hence the reaction was studied at $35^{\circ}C$ taking the overall concentrations of $K_2S_2O_8$, $AgNO_3$ and amide were 2.0×10^{-2} M, 2.0×10^{-3} M and 0.1 M respectively. The kinetic data of this run is recorded in B-1.

Table B-1

$$K_2S_2O_8 = 2.0 \times 10^{-2} M, \text{ Amide} = 0.1 \text{ M}, \text{ AgNO}_3 = 2.0 \times 10^{-3} M$$

$$\text{Temp} = 35^{\circ}C$$

Time	c^*	$k_1 \times 10^3 \text{min}^{-1}$
0	9.45	-
20	8.80	3.554
40	8.20	3.518
60	7.68	3.478
80	7.17	3.459
100	6.17	3.420
130	6.09	3.385
160	5.53	3.346
200	4.87	3.312
240	4.28	3.294
300	3.58	3.272
360	2.92	3.267
Mean $k_1 \times 10^3 \text{min}^{-1}$	-	3.391

$[c^*$ denotes the volume of $Na_2S_2O_3$ (0.02 M) in ml equivalent to unreacted $S_2O_8^{2-}]$

The data of the above table (Table B-1) show a fair in the first order rate constant values, suggesting that the overall order of the reaction at these concentrations of the reactants is unity. The concentration of amide is taken in excess and so the order is with respect to peroxydisulphate.

To decide conclusively the order w.r.t. $S_2O_8^{2-}$ and amide, another kinetic run was studied having equimolar concentrations (0.02 M each) of the two reactants. The results of these measurements are recorded in Table B-2.

Table B-2 : Amide = $K_2S_2O_8$ = 2.0 x 10^{-2}M,

AgNO$_3$ = 2.0 x 10^{-3}M, Tem = 35°C

Time (min)	C	k_1 x 10^3 min^{-1}
0	9.44	-
20	8.52	5.143
40	7.70	5.110
60	6.97	5.060
80	6.30	5.050
100	5.72	5.008
130	4.98	4.917
160	4.33	4.873
200	3.58	4.848
240	2.96	4.839
300	2.23	4.816
360	1.68	4.795
Mean k_1x10^3min^{-1}	-	4.950

Here again, fairly constant values of the first order specific rate are obtained, suggesting that the order w.r.t. $S_2O_8^{2-}$ is one.

EFFECT OF PEROXYDISULPHATE CONCENTRATION :

To investigate the effect of varying concentrations of $S_2O_8^{2-}$ ion on the reaction rate, three more kinetic runs having different concentrations of $S_2O_8^{2-}$ were carried out. Table B-3 contains the data of these kinetic runs. The kinetic data of Table B-1 have also been included in this table for the sake of comparison. These data also find a graphic representation in Fig. B-1. The values of the first order rate constant (viz. k_1) have been evaluated from the initial slope of the curves, shown in Fig. B-1, as well as calculated at different times by integration method. The corresponding values of the first order rate constants for the self decomposition of $S_2O_8^{2-}$ have been recorded directly as already mentioned in the experimental section of Chapter III.

Table B-3 : Amide = 0.1 M, $AgNO_3$ = 2.0 x 10^{-3}M, Temp-35°C

$[K_2S_2O_8]$ (M)	0.01		0.02		0.03		0.04	
Time(min)	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}
0	4.96	-	9.45	-	14.25	-	19.56	-
20	4.58	3.971	8.80	3.554	13.39	3.120	18.45	2.923
40	4.24	3.941	8.20	3.518	12.59	3.087	17.43	2.888
60	3.97	3.893	7.68	3.478	11.87	3.042	16.50	2.839
80	3.64	3.877	7.17	3.459	11.19	3.026	15.60	2.828
100	3.38	3.839	6.17	3.420	10.57	2.986	14.76	2.815
130	3.03	3.804	6.09	3.385	9.73	2.934	13.74	2.717
160	2.72	3.760	5.53	3.346	8.97	2.890	12.75	2.673
200	2.35	3.734	4.87	3.312	8.04	2.864	11.54	2.639
240	2.03	3.727	4.28	3.294	7.18	2.856	10.44	2.617
300	1.63	3.704	3.58	3.272	6.11	2.825	8.97	2.599
360	1.32	3.685	2.98	3.267	5.18	2.810	7.66	2.596
$k_1 \times 10^3$ min^{-1}	-	3.812	-	3.391	-	2.949	-	2.739
$k_2 \times 10^3$ min^{-1}	-	1.466	-	1.313	-	1.164	-	1.055
$k \times 10^3$ min^{-1}	-	2.346	-	2.078	-	1.785	-	1.684

An examination of the above results (Table B-3) it indicates that when the concentration of $S_2O_8^{2-}$ was increased, there is a decrease in the rate constant. It may also be seen that in any particular run, especially containing high concentration of $S_2O_8^{2-}$ the rate constant slightly decreases with time. This type of a behaviour of the reaction has been observed in the oxidation of amides as studied by Hambir Singh[180] and coworkers.

Now to study this effect under the conditions of constant ionic strength as well as at constant K^+ ion concentration, four kinetic runs having different concentrations of $S_2O_8^{2-}$ were studied, the data of which have been recorded in Table B-4 and shown graphically in Fig. B-2.

Table B-4 : Amide - 0.1 M, $AgNO_3$ = 2.0 x 10^{-3} M,

Temp = $35^{\circ}C$, μ = 0.301

$K_2S_2O_8(M)$	0.01	0.02	0.03	0.04
+ K_2SO_4 (M)	0.09	0.08	0.07	0.06
Time (min)	Vol.(in ml.)of 0.02 M-$Na_2S_2O_3$used(viz.C)			
0	4.95	9.45	14.34	19.52
20	4.65	8.92	13.67	18.69
40	4.37	8.44	13.05	17.91
60	4.12	7.99	12.48	17.21
80	3.88	7.57	11.93	16.53
100	3.66	7.19	11.44	15.91
130	3.38	6.65	10.75	15.06
160	3.12	6.17	10.13	14.28
200	2.80	5.57	9.33	13.26
240	2.50	5.02	8.75	12.32
300	2.12	4.32	7.59	11.05
360	1.79	3.72	6.72	9.90
k_1 x 10^3 min^{-1}	2.959	2.712	2.232	2.012
k_2 x 10^3 min^{-1}	0.73	0.72	0.70	0.70
k x 10^3 min^{-1}	2.229	1.992	1.532	1.312

A Comparison of the data given in the above table (Table B-4) with the data from Table B-3, shows that the decrease in the rate constant has been greatly minimized, suggesting that it was largely due to the increase in ionic strength as well as due to increase in ionic strength as well as due to increase in K^+ ion concentration, both causing inhibiting to the reaction (Fig. B-2). A slight decrease in the rate constant by increasing concentration of $S_2O_8^{2-}$ under these conditions, may be explained in a similar way as suggested in Chapter III.

Table B-5 shows the comparison between k values with increasing concentration of $[S_2O_8^{2-}]$ without K_2SO_4 and with K_2SO_4 to maintain constant ionic strength and constant K^+ concentration in the later case.

Table B-5 : Amide = 0.1 M, AgNO$_3$ = 2.0 x 10^{-3}M, Temp=35°C

Conc. $K_2S_2O_8$ without K_2SO_4 (M)	$k \times 10^3$ min^{-1}	Conc. $K_2S_2O_8$ with constant K^+ ionic strength (M)	$k \times 10^3$ min^{-1}
0.01	2.346	0.01	2.229
0.02	2.078	0.02	1.992
0.03	1.785	0.03	1.532
0.04	1.684	0.04	1.312

A plot of - log k versus concentration of $S_2O_8^{2-}$ is found to be linear as shown in Fig. B-3. The following

relationship between $-$ log k and concentration of $S_2O_8^{2-}$ is being followed.

$$- \log k = 2.575 + 5.413 \, [S_2O_8^{2-}]_0$$

Provided $[S_2O_8^{2-}] \neq$ Zero

ORDER WITH RESPECT TO PEROXYDISULPHATE :

To confirm the order w.r.t. $S_2O_8^{2-}$, the data of Table B-3 was subjected to vant Hoff's differential method. The volume of $Na_2S_2O_3$ (equivalent to $K_2S_2O_8$) was plotted against time for different initial concentrations of $K_2S_2O_8$. From these curves the value of $-\frac{dc}{dt}$ in each case was determined from the initial slope. The values are recorded in Table B-6.

Table B - 6

Conc. $K_2S_2O_8$ (M)	$-\frac{dc}{dt} \times 10^{-4}$	log $S_2O_8^{2-}$	$\log(-\frac{dc}{dt})$
0.01	1.752	$-$ 2.0000	$-$ 3.7565
0.02	3.700	$-$ 1.6990	$-$ 3.4318
0.03	5.112	$-$ 1.5229	$-$ 3.2915
0.04	7.225	$-$ 1.3979	$-$ 3.1411

The values of $-\frac{dc}{dt}$ and conc. $[S_2O_8^{2-}]$ are substituted in the Van't Hoffs equation, as given in case of the previous amide studied.

The values of $(-\frac{dc}{dt})$ for different initial concentrations of $S_2O_8^{2-}$ and the values of 'n' are calculated and recorded in Table B-7.

Table B - 7

$K_2S_2O_8$ (M)	$- dc/dt \times 10^{-4}$	Order of reaction (n)
0.01	1.752	
0.02	3.700	1.0786
0.01	1.752	
0.03	5.112	0.9748
0.01	1.752	
0.04	7.225	1.022
0.02	3.700	
0.04	7.225	0.9716
0.03	5.112	
0.04	7.225	1.1225

A plot of log -dc/dt versus log $S_2O_8^{2-}$ is shown in Fig. B-4. The slppe of the curve is 1.04. The order with respect to $S_2O_8^{2-}$ is one which is also confirmed by the values of n as shown in Table B-7.

EFFECT OF AMIDE CONCENTRATION :

To study the effect of amide concentration on the reaction rate, various kinetic runs, having different

amounts of reductant, were carried out. These results are recorded in Table B-8 and also shown graphically in Fig. B-5.

Table B-8 : $K_2S_2O_8$= 2.0 x 10^{-2}M, $AgNO_3$ = 2.0 x 10^{-3}M,
Temp = 35°C

Amide (M)	0.05	0.1	0.15	0.175	0.020
Time (Min)	Vol.(in ml.) of 0.02 M-$Na_2S_2O_3$ used(viz. C)				
0	9.43	9.45	9.45	9.46	9.45
20	8.80	8.80	8.78	8.78	8.80
40	8.23	8.20	8.17	8.16	8.20
60	7.71	7.68	7.61	7.60	7.66
80	7.21	7.17	7.09	7.07	7.15
100	6.78	6.17	6.62	6.61	6.70
130	6.19	6.09	6.03	5.96	6.11
160	5.65	5.53	5.47	5.40	5.55
200	5.00	4.87	4.80	4.71	4.89
240	4.41	4.28	4.20	4.11	4.29
300	3.37	3.58	3.45	3.36	3.35
360	3.06	2.92	2.83	2.75	2.94
k_1x10^3min^{-1}	3.266	3.391	3.495	3.560	3.395
k_2x10^3min^{-1}	1.313	1.313	1.313	1.313	1.313
k x10^3min^{-1}	1.953	2.078	2.182	2.247	2.082

From the above results as recorded in Table 3-8, it shows that the rate constants appears to be constant showing the zero order behaviour of the reaction.

The specific rate is seen to be a function of the initial concentration of $S_2O_8^{2-}$ and $CH_3.CH:CH.CONH_2$ governed by the expression.

$$k = k\, max \quad \cdot \quad \frac{(CH_3.CH:CH.CONH_2)_0}{b + (CH_3.CH:CH.\,CONH_2)_0}$$

In support of the above equation of a plot of $\dfrac{(CH_3\, .\, CH\, :\, CH\, .\, CONH_2)_0}{k}$ versus concentration of crotonamide is found to be linear (Fig. B-6) from which k max and b were evaluated as 0.002173 and 0.02717 from these values k is calcuatated and was found to be equal to 1.9096×10^{-3} which is identical with 2.078×10^{-3} the experimental value.

ORDER WITH RESPECT TO AMIDE :

In order to confirm the order with respect to amide, the kinetic data of Table B-8 were subjected to vant Hoff's differential method. From the initial slope of the concentration versus time curves, the values of $-dc/dt$ corresponding to various initial concentration of amide were evaluated which are given in Table B-9.

Table B - 9

conc. of Amide (M)	$-\frac{dc}{dt} \times 10^4$	log (Co)	Log(-dc/dt)
0.05	1.02	- 1.3010	- 3.9914
0.10	1.03	- 1.0000	- 3.9872
0.15	1.02	- 0.8239	- 3.9914
0.175	1.04	- 0.7569	- 3.9829
0.20	1.06	- 0.6021	- 3.9830

A plot of log (-dc/dt) versus log (amide concentration is shown in Fig. B-7. The value of the slope is zero, which suggests that the reaction is of zero order w.r.t. amide. Calculations were made for determining the order of reaction by using Vant[193] Hoff's differential method. These results are recorded in Table B-10.

Table B-10

Amide (M)	$(-\frac{dc}{dt}) \times 10^4$	Order of reaction (n)
0.05	1.02	0.01394
0.10	1.03	
0.05	1.02	0.00000
0.150	1.02	
0.05	1.02	0.01395
0.20	1.06	
0.10	1.03	0.0522
0.15	1.02	
0.10	1.03	0.07906
0.20	1.06	

From the above results as shown in Table B-10 it confirms that the order w.r.t. amide is zero.

EFFECT OF SILVER CATALYST CONCENTRATION :

In order to study the effect of different concentrations of the catalyst on reaction rate, the reaction was studied at five different concentrations of silver nitrate, keeping the concentrations of $K_2S_2O_8$ and amide unchanged. These results are recorded in Table B-11 and shown graphically in Fig. B-8.

Table B-11 : Amide = 0.1M, $K_2S_2O_8$ = 2.0 x 10^{-2}M,

Temp = 35°C

$(AgNO_3)$ x 10^{-3} M	1.0	1.5	2.0	3.0	4.0
Time (min.)	Vol.(in ml.)of 0.02 M-$Na_2S_2O_3$used(Viz.C)				
0	9.46	9.45	9.45	9.42	9.44
20	9.01	8.87	8.80	8.30	8.37
40	8.59	8.35	8.20	7.74	7.43
60	8.21	7.87	7.68	7.03	6.61
80	7.85	7.41	7.17	6.39	5.88
100	7.52	6.99	6.17	5.82	5.22
130	7.07	6.44	6.09	5.09	4.45
160	6.65	5.95	5.53	4.44	3.37
200	6.12	5.33	4.87	3.71	3.01
240	5.62	4.75	4.28	3.08	2.40
300	4.96	4.04	3.58	2.35	1.72
360	4.39	3.42	2.97	1.79	1.23
k_1 x 10^3 min^{-1}	2.261	2.960	3.391	4.764	5.817
k_2 x 10^3 min^{-1}	1.238	1.292	1.313	1.526	1.683
k x 10^3 min^{-1}	1.023	1.668	2.078	3.238	4.134

From the above results as shown in Table B-11 it indicates that, when the concentration of the catalyst was increased the reaction rate was also increased linearly. The plot of k versus [Ag] is shown in Fig. B-9. The following relationship is being followed :

$$k = 0.123 \times 10^{-3} + 1.00 \ [Ag^+]$$

EFFECT OF TEMPERATURE :

The reaction was studied at five different temperatures ranging from $25^{\circ}C$ to $45^{\circ}C$ with a view to determine the temperature coefficient, the energy of activation and other energy parameters. Table B-12 contains the results of these kinetic runs and also shown graphically in Fig. B-10.

Table B-12 : Amide = 0.1 M, $K_2S_2O_8$=2.0 x 10^{-2}M, $AgNO_3$ = 2.0 x 10^{-3}M

Temperature $^\circ C$	25	30	35	40	45
Time (min)	Vol.(in ml.)of 0.02 M-$Na_2S_2O_3$used(viz.C.)				
0	9.45	9.46	9.45	9.44	9.42
20	9.07	8.98	8.80	8.55	8.27
40	8.73	8.54	8.20	7.75	7.26
60	8.41	8.14	7.68	7.05	6.37
80	8.09	7.75	7.17	6.41	5.60
100	7.82	7.40	6.17	5.83	4.93
130	7.46	6.95	6.09	5.08	4.10
160	7.14	6.52	5.53	4.43	3.40
200	6.67	5.97	4.87	3.68	2.65
240	6.22	5.45	4.28	3.06	2.05
300	5.64	4.78	3.58	2.32	1.41
360	5.12	4.20	2.92	1.76	0.97
k_1 x 10^3 min^{-1}	1.843	2.405	3.391	4.785	6.464
k_2 x 10^3 min^{-1}	0.750	0.900	1.313	1.653	2.561
k x 10^3 min^{-1}	1.093	1.505	2.078	3.132	3.903

The calculated values of $\frac{1}{T} \times 10^3$ and $\log \left[\frac{kr}{kT/h} \right]$ are shown in Table B-13.

Table B-13

Temp. A^o	$\frac{1}{T} \times 10^3$	kr x 10^3 min^{-1}	log kr	$\log \left[\frac{kr}{kT/h} \right]$
298	3.356	1.093	- 2.9614	- 15.7735
303	3.301	1.505	- 2.8225	- 15.6468
308	3.246	2.078	- 2.6845	- 15.4150
313	3.196	3.132	- 2.5042	- 15.3424
318	3.145	3.903	- 2.4087	- 15.2540

An examination of the above data (Table B-13) it indicates that the specific rate is nearly doubled for 10^oC rise in temperature. A plot of log k versus 1/T is found to be linear (Fig. B-11) showing that the reaction obeys Arrhenius relationship.

The energy of activation from the slope of the curve is 12.666 K.Cals. mole^{-1} which is in good agreement with the calculated value 12.572 K.Cals Mole^{-1}. Similarly from the slope of the curve obtained by plotting log ($\frac{kr}{kT/h}$) versus 1/T (Fig. B-12) the value of the enthalpy change for the formation of activated complex ($H^{\neq}$) is calculated. These values of E and $H^{\neq}$ have been recorded in Table B-14 alongwith those of other thermodynamic parameters.

Table B-14

Temperature	$k \times 10^3$ min^{-1}	Temp coefficient	E K.Cals. mole^{-1}	A $\times 10^4$ litre mole^{-1} Sec^{-1}	$\Delta G^{\neq}$ K.Cals. mole^{-1}	$\Delta S^{\neq}$ E.U.	$\Delta H^{\neq}$ K.Cals. mole^{-1}
298	1.093	-	-	2.677	21.642	- 32.642	
303	1.505	1.892	11.630	2.602	21.898	- 32.58	
308	2.078	2.08	13.727	2.555	22.485	- 32.64	11.721 (gra-
313	3.132	1.887	12.359	2.791	20.478	- 32.14	phically)
318	3.903	-	-	2.535	22.803	- 32.68	
Mean	-	1.953	12.572	2.632	21.861	- 32.50	

A large negative value of entropy of activation is indicative of the formation of an activated complex involving either two oppositely charged ions or an ion and a neutral molecule.

The rate constant for this reaction may be expressed by the following relation :

$$k = 2.632 \times 10^4 . e^{- 12.572/RT} \; Sec^{-1}$$

EFFECT OF IONIC STRENGTH :

The effect of varying ionic strength on the reaction rate was studied by the addition of different amounts of K_2SO_4 to the reaction mixture. The results of these kinetic runs are recorded in Table B-12 and shown graphically in Fig. B-12.

Table B-15 : Amide = 0.1M, $K_2S_2O_8$=2.0 x 10^{-2}M,

AgNO$_3$ = 2.0 x 10^{-3}M, Temp = 35°C

$[K_2SO_4]$ (M)	Nil	0.005	0.01	0.015	0,02	0.03	0.04
μ	0.061	0.076	0.091	0.106	0.121	0.151	0.181
Time (min)	Vol.(in ml)of 0.02 M-Na$_2$S$_2$O$_3$ used (viz.c)						
0	9.45	9.45	9.48	9.46	9.48	9.46	9.46
20	8.80	8.82	8.90	8.90	8.94	8.95	9.02
40	8.20	8.25	8.36	8.38	8.45	8.48	8.61
60	7.68	7.72	7.87	7.91	8.00	8.06	8.24
80	7.17	7.23	7.41	7.47	7.56	7.64	7.88
100	6.17	6.79	7.00	7.06	7.18	7.27	7.56
130	6.09	6.21	6.46	6.56	6.67	6.77	7.15
160	5.53	5.70	5.94	6.06	6.17	6.31	6.75
200	4.87	5.02	5.33	5.45	5.54	5.73	6.24
240	4.28	4.40	4.73	4.89	5.00	5.20	5.73
300	3.58	3.70	4.03	4.18	4.28	4.51	5.12
360	2.92	3.07	3.40	3.36	3.67	3.90	5.54
k_1x 10^3min^{-1}	3.391	3.258	2.985	2.863	2.759	2.591	2.185
k_2x 10^3min^{-1}	1.313	1.292	1.235	1.180	1.163	1.125	0.850
k x 10^3min^{-1}	2.078	1.966	1.693	1.683	1.596	1.466	1.335

From the above results as shown in Table B-15 it indicates that the salt effect is negative and the reaction retains its first order character.

On plotting log k against $(\mu)^{1/2}$ as well as k against μ as shown in Fig. in 14(A) and 14(B) respectively. It is found that log k versus $(\mu)^{1/2}$ curve is linear in the region of low ionic strength (< 0.20) while there exists no linearity in the plot of k versus μ. This suggests that the salt effect is of primary exponential type in the region of low ionic strength indicating that the rate determining process involves a reaction between two oppositely charged ions.

Table B-16

K_2SO_4(M)	μ	$k \times 10^3 min^{-1}$	$\sqrt{\mu}$	log k
0.000	0.008	2.078	0.08944	- 2.6825
0.005	0.023	1.966	0.1517	- 2.6998
0.01	0.038	1.693	0.1949	- 2.7714
0.015	0.053	1.683	0.2302	- 2.7740
0.02	0.068	1.596	0.2607	- 2.7970
0.03	0.098	1.466	0.3130	- 2.8338
0.04	0.128	1.325	0.3578	- 2.8746

It may be stated that the ionic strength employed
is rather high for Bronsted relationship to be strictly
quantitatively applicable but still the agreement is
found to be fairly good.

SPECIFIC IONIC EFFECT :

In order to study the effects of various salts on
the reaction rate the reaction was studied by the addition
of different salts in the reaction mixture. This study
has been carried out at constant ionic strength. The
results of these kinetic runs are recorded in Table B-17
and shown graphically in Fig. B-15.

Table B-17 : Amide = 0.1 M, $K_2S_2O_8$ = 2.0 x 10^{-2}M,

AgNO$_3$ = 2.0 x 10^{-3} M, Temp = 35°C, μ = 0.211

Salt added	No Salt	K_2SO_4	Na_2SO_4	Li_2SO_4	$MgSO_4$	$ZnSO_4$
Concentration (M)	0.00	0.05	0.05	0.05	0.0375	0.0375
Time (Min)	Vol.(in ml.) of 0.02 M-Na$_2$S$_2$O$_3$used (viz.C)					
0	9.45	9.45	9.45	9.46	9.48	9.46
20	8.80	9.03	8.99	8.95	8.93	8.88
40	8.20	8.64	8.56	8.47	8.44	8.34
60	7.68	8.33	8.18	8.04	7.98	7.85
80	7.17	7.94	7.80	7.63	7.54	7.39
100	6.17	7.62	7.46	7.26	7.15	6.97
130	6.09	7.24	6.98	6.74	6.64	6.45
160	5.53	6.86	6.55	6.28	6.15	5.94
200	4.87	6.36	6.00	5.69	5.56	5.32
240	4.28	6.32	5.49	5.15	5.00	4.74
300	3.58	5.27	4.83	4.46	4.29	4.02
360	2.92	4.71	4.23	3.85	3.67	3.40
k_1 x 10^3min^{-1}	3.391	2.072	2.342	2.619	2.753	2.991
k_2 x 10^3min^{-1}	1.313	0.850	0.860	0.880	0.920	0.960
k x 10^3min^{-1}	2.078	1.222	1.382	1.739	1.833	2.031

It is seen that the specific inhibitory effect of the various ions is in the order

$$K^+ > Na^+ > Li^+ > Mg^{2+} > Zn^{2+}$$
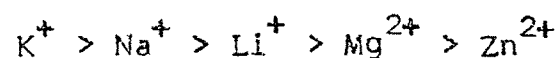
EFFECT OF HYDROGEN ION CONCENTRATION :

In order to study whether the reaction is affected when the pH of the reaction system is changed, the reaction was studied at different H^+ ion concentrations by the addition of sulphuric acid. These results are recorded in Table B-18 and shown graphically in Fig. B-16.

Table B-18 : Amide = 0.1 M, $K_2S_2O_8$ = 2.0 x 10^{-2} M,

AgNO$_3$ = 2.0 x 10^{-3}M, Temp = 35°C

H$_2$SO$_4$ (M)	Nil	0.025	0.05	0.075	0.1
Time (min)	Vol.(in ml.) of 0.02 M-Na$_2$S$_2$O$_3$ used(Viz.C)				
0	9.45	9.48	9.52	9.52	9.48
20	8.80	8.94	9.00	9.03	9.06
40	8.20	8.43	8.51	8.53	8.68
60	7.68	7.98	8.07	8.16	8.33
80	7.17	7.54	7.65	7.76	7.98
100	6.17	7.15	7.27	7.41	7.68
130	6.09	6.61	6.76	6.95	7.24
160	5.53	6.13	6.30	6.51	6.84
200	4.87	5.53	5.71	5.95	6.33
240	4.28	4.97	5.17	5.43	5.85
300	3.58	4.26	4.47	4.75	5.23
360	2.92	3.64	3.85	4.16	4.66
k_1 x 10^3 min^{-1}	3.391	2.785	2.648	2.451	2.089
k_2 x 10^3 min^{-1}	1.313	0.980	0.870	0.780	0.680
k x 10^3 min^{-1}	2.078	1.805	1.778	1.671	1.409

From the above results (Table B-18), it is seen that the rate of the reaction is affected by the change in pH of the reaction mixture. Lowing of pH results in the decrease of the rate constant. Now it is possible that this decrease in the rate of the reaction may not be due to a change in the pH but may be due to an increase in the ionic strength resulting by the addition of H_2SO_4.

To varify which of the possibilities hold good, the effect was reinvestigated at constant ionic strength by adding the mixture of K_2SO_4 and H_2SO_4 so as to maintain the ionic strength of the reaction mixture constant. The kinetic results of these runs are recorded in Table B-19 and shown graphically in Fig. B-17.

Table B-19 : Amide = 0.1 M, $K_2S_2O_8$ = 2.0 x 10^{-2}M,

AgNO$_3$ = 2.0 x 10^{-2}M, Temp = 35°C,

μ = 0.361

H_2SO_4 (M) + K_2SO_4 (M)	Nil 0.100	0.025 0.075	0.05 0.05	0.075 0.025	0.100 Nil
0	9.52	9.53	9.52	9.48	9.48
20	9.14	9.14	9.11	9.07	9.06
40	8.80	8.79	8.74	8.70	8.68
60	8.48	8.46	8.40	8.36	8.33
80	8.17	8.14	8.07	8.02	7.98
100	7.89	7.86	7.78	7.72	7.68
130	7.56	7.50	7.37	7.30	7.24
160	7.21	7.13	7.00	6.93	6.84
200	6.77	6.67	6.51	6.43	6.33
240	6.33	6.22	6.04	5.96	5.85
300	5.76	5.64	5.42	5.35	5.23
360	5.23	5.09	4.86	4.78	4.66
k_1 x 10^3 min^{-1}	1.813	1.935	1.995	2.020	2.089
k_2 x 10^3 min^{-1}	0.610	0.630	0.640	0.650	0.680
k x 10^3 min^{-1}	1.203	1.305	1.355	1.370	1.409

From the above results (Table B-19) it is seen that the rate of the reaction is increased by increasing H^+ ion concentration (and obviously decreasing K_2SO_4 concentration). This suggests that either the reaction may be catalysed by H^+ ions or both K^+ and H^+ ions have specific inhibitory effect and that the specific inhibitory effect of K^+ ion is greater than that of H^+ ions. A sharp fall in the reaction rate by increasing the H^+ ion concentration rules out (Table B-18) the possibility that the increase in the rate constant values at constant ionic strength (Table B-19) is brought about due to catalytic effect of H^+ ions, leaving, thus only to conclude that K^+ ions cause inhibition of greater magnitude in comparison to that brought about by H^+ ions and that the observed increase in the rate constant at constant ionic strength (Table B-19) is due to increasing proportion of H_2SO_4 at the expense of equimolar concentrationof K_2SO_4.

EFFECT OF ALLYL ACETATE :

To study the effect of allyl acetate on the reaction rate, the reaction was studied in the absence of and at three different initial concentrations of allyl acetate. The results of these kinetic runs are recorded in Table B-20 and shown graphically in Fig. B-18.

Table B - 20 : Amide = 0.1 M, $K_2S_2O_8$ = 2.0 x 10^{-2} ,

AgNO$_3$ = 2.0 x 10^{-3}M, Temp=35°C

Allyl acetate	0.00	0.001	0.005	0.01
Time (min)	Vol.(in ml)of 0.02 M-Na$_2$S$_2$O$_3$used(viz.C)			
0	9.45	9.48	9.46	9.45
20	8.80	9.12	9.16	9.20
40	8.20	8.78	8.89	8.98
60	7.68	8.49	8.64	8.77
80	7.17	8.19	8.39	8.56
100	6.17	7.93	8.17	8.39
130	6.09	7.55	7.87	8.18
160	5.53	7.21	7.60	7.96
200	4.87	6.77	7.23	7.67
240	4.28	6.35	6.87	7.37
300	3.58	5.79	6.38	6.97
360	2.92	5.27	5.93	6.60
k x 10^3 min^{-1}	3.391	1.760	1.428	1.140

From the above results (Table B-20) it is seen that allyl acetate inhibits the rate of reaction, so the reactions involving $S_2O_8^{2-}$ are greatly inhibited by allyl acetate which acts as sulphate radical capture agent. In this case allyl acetate does not act as a very efficient radical capture reagent. The radical capture may be due to the polymerization of allyl acetate by sulphate ions formed from the catalysed decomposition of peroxydisulphate.

MOLE RATIO :

To determine the number of moles of $S_2O_8^{2-}$ reacting with one mole of amide, graphical method was employed. $K_2S_2O_8$ was taken in excess as compared to amide along with a fixed concentration of amide and silver catalyst. Simultaneously a blank run was also carried out. At suitable intervals of time 5 ml of the reaction mixture was pipetted out and estimated for unreacted $S_2O_8^{2-}$. The results obtained are recorded in Table B-21 and shown graphically in Fig. B-19.

Table B - 21

Reaction mixture $=$ Overall concentration

$K_2S_2O_8$ $=$ 0.05 M

$AgNO_3$ $=$ 0.001 M

Temperature $=$ $35^{\circ}C$

Amide(M)	0.01 M	0.00M
Time (min)	Vol. (in ml.) of 0.02 M-$Na_2S_2O_3$ used (viz.C)	
0	24.46	24.13
30	23.10	23.45
60	22.00	22.33
90	19.94	21.42
120	18.60	20.90
150	17.32	20.47
180	16.37	19.58
210	15.25	19.14
240	13.91	18.23
270	13.28	17.36
300	12.50	16.95
330	11.73	15.84
360	11.31	15.80
390	10.69	15.10
420	10.52	14.46
450	9.92	14.21
480	9.41	13.56

The curve consists of two portions - the first for the oxidation of amide and second for the self decomposition of $S_2O_8^{2-}$ ion. Now tangents are drawn on portions of the curve which intersect at point P. From this point of intersection, the value of $K_2S_2O_8$ consumed in the complete oxidation of 5 ml of 0.01 amide is calculated. The point Q on the curve at the same time gives the value corresponding to self decomposition of $K_2S_2O_8$.

From the graph as shown in Fig B-19 It is seen that the two plots become parallel at P. At this point log C = 1.05 which corresponds to 11.22 ml.

The corresponding value of log C at the same time on the self decomposition the curve is shown by the point Q. At this point log C = 1.021 which corresponds to 16.21 ml. The difference between two values is 4.99 ml.

Therefore, 4.99 ml
of 0.02-N $Na_2S_2O_3$ = 4.99 ml of 0.02 N $K_2S_2O_8$

= 4.99 ml of 0.01 M $K_2S_2O_8$

Hence 5 ml of 0.01 M amide

= 4.99 ml of 0.01 M $K_2S_2O_8$.

Thus one mole of amide consumes one mole of $K_2S_2O_8$ for the completion of reaction.