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RESEARCH ARTICLE

A KINETIC STUDY OF THE OXIDATION OF NITRITE ION BY PEROXODISULPHATE.

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Abstract

The oxidation of nitrite ion NO_2^- by Peroxodisulphate ion $S_2O_8^{2-}$ was studied in high ionic strength and in phosphate and acetate media at around pH=7 and 60^0C . Under controlled conditions the reaction is of overall second order being first order with respect to reactants. Cations (Na^+, K^+, Ca^{+2}, Mg^{+2} and Cu^{+2} catalyze the reaction and the extent of catalysis depends on the nature and concentration of the cations.The temperature effect on the redox reactions was studied and the activation energy is 60.01 $kJmol^{-1}$. The mechanism has been proposed. Based on experimental data and kinetic simulation, we have modified previous models for this reaction mechanism and show that the new model proposed here is consistent with experimental data. The stoichiometry was determined to be:-

$$S_2O_8^{2-} + NO_2^- \longrightarrow 2SO_4^{2-} + NO_3^- + 2H^+ \qquad (1)$$

And the experimental rate law is:

$$R_0=k_1[S_2O_8^{2-}]_0+k_2^0[S_2O_8^{2-}]_0\,[NO_2^-]_0+\{\Sigma k_{Mi}^{n+}[M^{n+}]\}[S_2O_8^{2-}]_0[NO_2^-]_0 \qquad (2)$$

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Introduction:-

Peroxodisulphate ion $S_2O_8^{2-}$ 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(2,3). Many studies on the thermal decomposition of Peroxodisulphate ions were made by many workers such as Cotton, Kolthoff, Miller, Vasudeva, Taha and Wasif(4) and there is general agreement that it follows first order kinetics. Reactions involving peroxodisulphate ion are generally slow at ordinary temperatures(5) 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 nitrite ion.

The kinetic study of the reaction of nitrite ion has been of increasing interest due to its biological and chemical implications(6,7). Nitrite ion is a common contaminant in water, and because its complexing ligand (with Fe(II))its presence can be dangerous. The kinetics of the redox reaction of $S_2O_8^{2-}$ and NO_2^- was studied by a number of workers. Elamin(8,9), who found that the oxidation of nitrite ion by peroxodisulphate was second order, being first order with each reactant.

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Materials:-

All chemicals used are of high purity (98%). The redox reaction of peroxodisulphate with nitrite ion proceeds at measurable rate at about 60^0C and it is for this reason, that the temperature range 60^0- 75^0C 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 $NaNO_2$, added salts ($NaNO_3$ and KNO_3) which maintained the constant ionic strength and phosphate buffer (Na_2HKPO_4 – KH_2PO_4). Also solutions A and B were prepared in the same manner and acetate ($C_2H_3O_2Na$ – $C_2H_4O_2$) buffer is used instead of phosphate buffer. 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:-

(i) Solution A: Calculated amount of $K_2S_2O_8$ (A.R) was dissolved in double distilled water to make 500cm^3 of solution A.

(ii) Solution B: Calculated amount of $NaNO_2$, $NaNO_3$, KNO_3 and Phosphate buffer (Na_2HPO_4 - KH_2PO_4) or acetate buffer ($C_2H_3O_2Na$ – $C_2H_4O_2$) are dissolved in double distilled water to make 500cm^3 of solution B. The additional components under study (i.e. allylacetate was added in each kinetic run to solution B.

Reaction Conditions:-

The redox reaction was carried out in the conditions: $[S_2O_8^{2-}]_0=[NO_2^-]_0$, high ionic strength around one (I=0.80-1.34), Phosphate buffer $[Na_2HPO_4]=[KH_2PO_4]=0.20$ mol dm^3 or acetate buffer (Na_2HPO_4 - KH_2PO_4).

Kinetic measurements:-

The progress of the reaction was followed by examining the concentration of peroxodisulphate ion at various time interval. The concentration of $S_2O_8^{2-}$ was determined iodometrically during the kinetic run. Purified nitrogen gas was passed through the quenched iodine flask contain 10cm^3 sample so as to drive away any dissolved oxygen. Then 4gms of KI ware added. It was then placed in the dark for about 10minutes till all the iodine was liberated. The liberated iodine was then titrated against standard sodium thiosulphate using starch as an indicator.

The concentration of nitrite ion was determined before the kinetic runs by two methods;

(a) Titration method: By using standard potassium permanganate solution.

(b) Spectrophotometric method: By reacting nitrite ion with a series of organic materials to form a purple dye, so that the measured absorption A was plotted vs. nitrite concentration. A straight line passing through the original point was obtained and thus providing that the solution obeys Beer's law.

Results and Discussion:-

Kinetic order with respect to Peroxodisulphate ion

The order of the reaction-in its initial stages-with respect to $S_2O_8^{2-}$ was investigated under the constant conditions given in the captions of table (1) which shows the variation of the initial rate of disappearance of peroxodisulphate ion,R_0, with its initial concentrations. A plot of R_0 vs. $[S_2O_8^{2-}]_0$ (fig.1) gives a straight line indicating that the reaction is first order with respect to $S_2O_8^{2-}$, thus:

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

Where k_{obs} is initial-pseudo first order rate constant. From fig(1) the slope = k_{obs} = 3.7398X10^{-5} s^{-1} , at 60^0C.

Table (1) Variation of R_0 with $[S_2O_8^{2-}]_0$

$[NO_2^-]_0$=0.0752 mol dm^{-3} $[Na^+]=[K^+]$=0.500 mol dm^{-3}
$[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3} I=1.23-1.26
pH=6.47 Temp.=60^0C

$[S_2O_8^{2-}]_0$ / mol dm^{-3}	0.0085	0.0165	0.0283	0.0375	0.0850
10^5xR_0/mol dm^{-3} min^{-1}	1.8771	3.4502	6.2727	8.3648	18.000

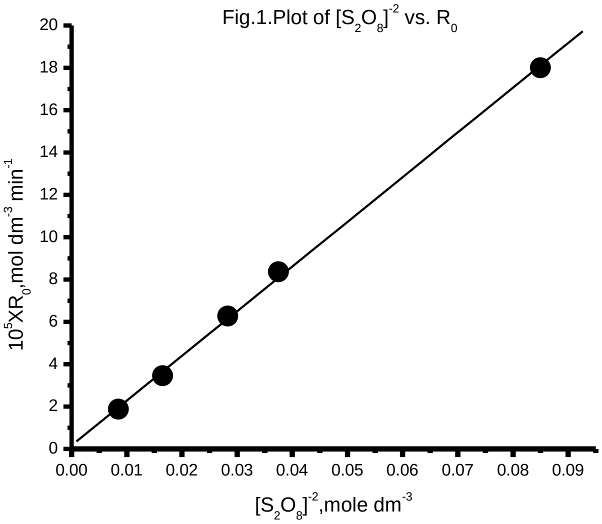
Fig.1.Plot of $[S_2O_8]^{-2}$ vs. R_0

Kinetic order with respect to Nitrite ion:-

The effect of varying the initial concentration of nitrite ion –while- keeping $[S_2O_8^{2-}]_0$ and other factors constant, was investigated by plotting of initial rate of the disappearance of peroxodisulphate against the respective $[NO_2^-]_0$ values, (fig 2) and (Table 2), a straight line intercepting the y-axis was obtained suggesting a rate equation of the form:

$R_0 = -d[S_2O_8^{2-}]_0/dt = R_1 + k[NO_2^-]_0$ (2)

R_1 represents the thermal decomposition of peroxodisulphate in the absence of nitrite ion while the second term represents the redox $(S_2O_8^{2-}\text{-}NO_2^-)$path. Since the reaction is first order in $S_2O_8^{2-}$ equation (2) can be rewritten as:

$R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0\ [NO_2^-]_0$ (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 $[NO_2^-]_0$

$[S_2O_8^{2-}]_0$=0.0751 mol dm^{-3} [Na+]=[K+]=0.500 mol dm^{-3}
$[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3} I=1.23-1.27
pH=6.47 Temp.=60^{0}C

$[NO_2^-]_0$ / mol dm^{-3}	0.0100	0.0350	0.0500	0.0750	0.1000
10^5xR_0/mol dm^{-3} min^{-1}	4.1489	8.9667	12.1277	16.3176	21.7895

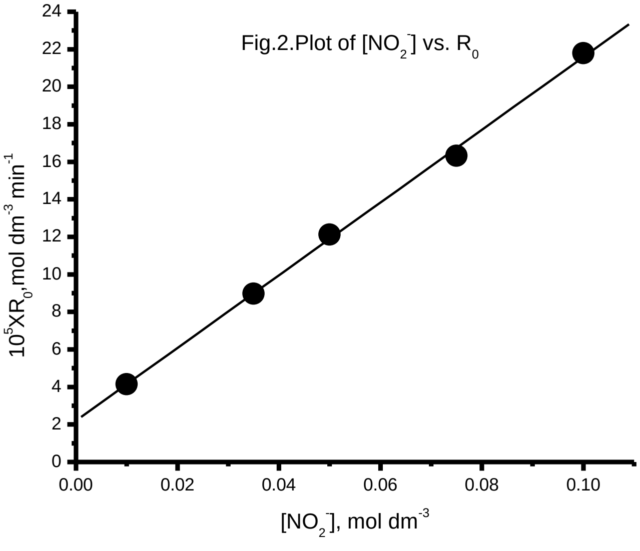
Fig.2.Plot of $[NO_2^-]$ vs. R_0

Effect of hydrogen ion:-

The pH of the redox reaction was changed in the range (4.65-8.41) by changing the ratio $[HPO_4^{2-}]/[H_2PO_4^-]$ under otherwise constant experimental conditions table(3). The pH was measured directly using a pH-meter. From table (3.3) there is no clear effect on R_0. Therefore it is safe to conclude that the rate of the reaction is independent of pH.

Table (3) Variation of R_0 with pH:-

$[S_2O_8^{2-}]_0$=0.0750 mol dm^{-3} $[NO_2^-]_0$=0.0748 mol dm^{-3}

$[Na^+]=[K^+]$=0.500 mol dm^{-3} $[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3} I=1.1-1.2

Temp.=60^{0}C

10^{-7}x[H$^+$], mol dm^{-3}	pH	10^4xR$_0$/mol dm^{-3} min^{-1}
22.284	4.652	1.620
15.030	5.823	1.632
1.1939	6.923	1.650
0.1321	7.879	1.688
0.0389	8.409	1.711

Effect of free radical scavengers:-

The effect of adding allylacetate in multi concentrations was studied by carrying out the runs in experimental conditions given in the caption of table (4). From this table no clear effect is observed. This probably shows that free radicals are not involved in the rate-determining step although the result does not exclude the presence of free radicals in other fast steps.

Table (4) Variation of R_0 with Allyl acetate:-

$[S_2O_8^{2-}]_0$=0.0750 mol dm^{-3} $[NO_2^-]_0$=0.0750 mol dm^{-3}

[Na+]=[K+]=0.500 mol dm^{-3} $[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3} I=1.24 pH=6.47

Temp.=60^{0}C

10^3x[Allyl acetate] / mol dm^{-3}	Nil	6.1892	9.2193	11.2371
10^5xR$_0$/mol dm^{-3} min^{-1}	2.778	2.768	2.759	2.776

Effect of added salts:-

The effect of added the salts $NaNO_3$,KNO_3 , $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Cu(NO_3)_2$ on the redox reaction was shown in figs.(3and 4) by varying the concentration of the cation under otherwise constant experimental conditions given in tables (5 and 6). To investigate the effect of divalent cations (Mg^{+2} , Ca^{+2} and Cu^{+2}) the medium was changed from phosphate buffer to acetate buffer which does not form precipitates with the cations. Effect of Na^+ and K^+ were repeated in acetate medium. It is clear from figs.(3and 4) that the rate of the reaction is linearly to cations concentrations ($[M^{+n}]$, n=1or 2), thus the rate of the reaction may be expressed by eq.4.

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

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

$$C = k_1[S_2O_8^{2-}]_0 + k_2^0[S_2O_8^{2-}]_0[NO_2^-]_0 + k_{Mi}^{+n}[M_i^{+n}][S_2O_8^{2-}]_0[NO_2^-]_0 \quad (5)$$

$$k_{obs} = k_M^{+n}[S_2O_8^{2-}][NO_2^-] \quad (6)$$

where k_M^{+n} is the catalytic rate constant for the cation M^{+n} under study, k_{Mi}^{+n} is that of the residual cation M^{+n} 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 is 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 $Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Cu^{2+}$.

Fig. 3. Effect of added Na^+ and K^+ in phosphate medium

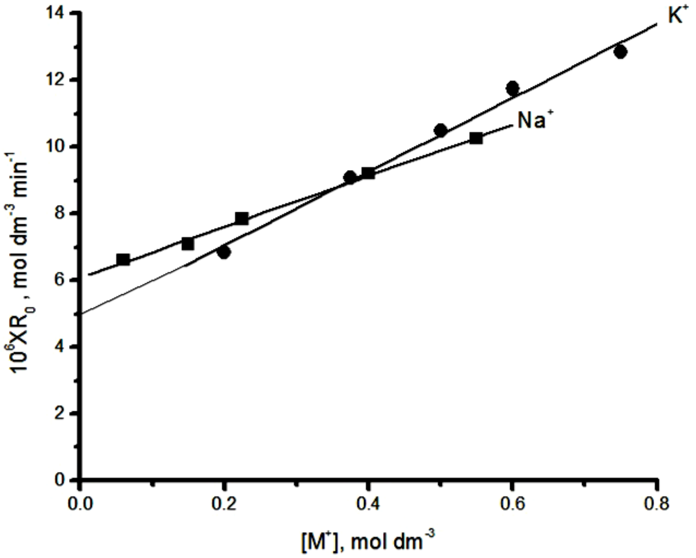

Fig. 4. Effect of added Mg^{2+} , Ca^{2+} and Cu^{2+} in acetate medium

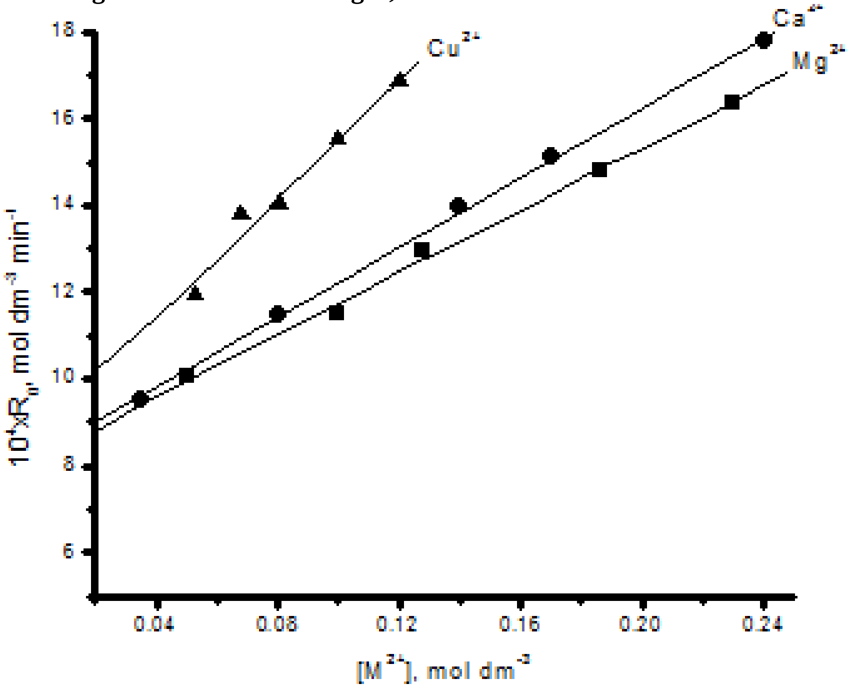

Table (5)Effect of added Na^+ and K^+ cations in phosphate medium

$[S_2O_8^{2-}]_0$=0.0750 mol dm^{-3} $[NO_2^-]_0$=0.0750 mol dm^{-3}

$[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3} pH=6.47 Temp.=60^{0}C

Cation	$k_M^+ x10^4$ mol^{-2} dm^6 s^{-1}
Na^+	2.80±0.06
K^+	4.52±0.04

Table (6)Effect of added Na^+ , K^+ , Mg+2 ,Ca+2 and Cu+2 cations in acetate medium

$[S_2O_8^{2-}]_0$=0.0650 mol dm^{-3} $[NO_2^-]_0$=0.0650 mol dm^{-3} $[C_2H_3O_2Na]=[C_2H_4O_2]$=0.20 mol dm^{-3} pH=4.67 Temp.=60^{0}C

Cation	**Cx10^6(intercept) mol dm^3 s^{-1}**	**k_{obs}x10^6 s^{-1}**	**k_M^{+n}x10^4 mol^{-2} dm^6 s^{-1}**	**K_2^0x10^5 mol^{-1} dm^3 s^{-1}**
Na^+	1.03	1.25	2.91±0.04	4.31
K^+	0.77	1.94	4.54±0.03	4.01
Mg^{+2}	1.35	5.92	13.84±0.09	4.35
Ca^{+2}	1.36	6.75	15.80±0.01	4.35
Cu^{+2}	1.36	11.88	27.50±0.08	4.36

The rate law for the reaction is thus detailed as in equation (7).

$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0 [NO_2^-]_0 + \{\Sigma k_{Mi}^{n+}[M^{n+}]\}[S_2O_8^{2-}]_0 [NO_2^-]_0 \qquad (7)$$

Where k_{Mi}^{n+} is the catalytic rate constant for ith ion.

Where i = 1,2 represents the cations present in the system. When only one cation is present the term within the Σ sign reduces to $k_M^{n+}[M^{n+}]$ and equation becomes:

$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2[S_2O_8^{2-}]_0 [NO_2^-]_0 + k_M^{n+}[M^{n+}]\}[S_2O_8^{2-}]_0 [NO_2^-]_0 \qquad (8)$$

Effect of temperature:-

The effect of temperature on the k_2 path was studied over the temperature range 60-75C^0 at otherwise constant experimental conditions of:

$[S_2O_8^{2-}]_0$ =0.0660 mol dm^{-3} , $[NO_2^-]_0$ = 0.0663 mol dm^{-3}

[Na+]=[K+] = 0.50 mol dm^{-3} , $[HPO_4^{2-}]=[H_2PO_4^-]$=0.20 mol dm^{-3}

I=1.24 pH=6.47

The values of the first order rate constant for the thermal decomposition of $S_2O_8^{2-}$,k_1, calculated by Elamin, were used in calculating k_2 at each temperature from eqation(5). Results are summarised in table(7).

The effect of temperature on k_2 components (i.e.k_2^0 and k_M^{+n}) was also studied in the range 60-75^{0}C. For each temperature k_2 was calculated from equation(**3**), and then k_M^{+n} was calculated from y-intercept of figures resulting from plot of $[M^{+n}]$ vs.R_0 by using the equation

$$R_0 = k_1[S_2O_8^{2-}]_0 + k_2^0[S_2O_8^{2-}]_0 [NO_2^-]_0 + k_M^{n+}[M^{n+}][S_2O_8^{2-}]_0 [NO_2^-]_0 \qquad (9)$$

From plot of logk_{Mn}^+ against 1/T the relevant Arrhenius parameters are calculated in table (7) for each path.

Table (7) Thermodynamics parameters of activation

Path	ΔE$^\#$/kJmol^{-1}	A	ΔS$^\#$/JK^{-1}	ΔG$^\#$/kJmol^{-1}
K_2	60.01	7.64x10^5	132.97	14.54
K_2^0	98.74	1.26x10^{11}	33.23	87.68
k_{Na}^+	74.70	1.56x10^8	88.73	45.15
k_K^+	66.40	1.34x10^7	109.03	30.09

Discussion:-

A proposed mechanism:-

The rate law equation(2) may be explained by the following mechanism:

Path(I): Thermal decomposition of peroxodisulphate independent of nitrite ion which has its rate-determining step in equation(6)

$$S_2O_8^{2-} \quad k_1 \longrightarrow 2SO_4^{-\cdot} \qquad \text{slow} \qquad (10)$$

Therefore the rate equation of this path may represent by the equation(7)

$$\text{Rate} = k_1 [S_2O_8^{2-}]_0 \qquad (11)$$

Which corresponds to the right hand side (r.h.s.) of equation (2).

Some $SO_4^{\cdot}$ radicals seem to end up forming oxygen according to well established mechanism discussed by House$^{(10)}$, while most $SO_4^{\cdot}$ radicals seem to oxidize NO_2^- ion in some faster steps represented by the overall equ.(8) given by Elamin$^{(7)}$.

$$2SO_4^{-\cdot} + NO_2^- + H_2O \longrightarrow 2SO_4^{2-} + NO_3^- + 2H^+ \qquad (12)$$

Path(II): In this path the rate determining step involves both $S_2O_8^{2-}$ and NO_2^- which in presence of water leads to products as:

$$S_2O_8^{2-} + NO_2^- + H_2O \xrightarrow{k_2} [S_2O_8^{2-}.NO_2^-] \xrightarrow{\text{fast}} 2SO_4^{2-} + NO_3^- + 2H^+ \qquad (13)$$

which the rate equation:
$-d[S_2O_8^{2-}]_0/dt = k_2[S_2O_8^{2-}]_0 [NO_2^-]_0$ (14)
and this explains the second term on the r.h.s. of equation(2)

Path(III): Because of the divalent negative charge of $S_2O_8^{2-}$ ion forms an ion-pair with the cation (in preference to the monovalent NO_2^-) in fast equilibrium represented by equation(11):
$M^{n+} + S_2O_8^{2-} \overset{K_e}{\rightleftharpoons} MS_2O_8^{n-2}$ (15)

Which gives $K_e = [MS_2O_8^{n-2}] / [M^{n+}][S_2O_8^{2-}]$ (16)
Nitrite ion is expected to reacts with the ion-pair faster than its reaction with the un-associated $S_2O_8^{2-}$ ion(11,12) due to the decrease of coulumbic barrier. The resulting activated complex formed by the interaction between NO_2^- and $MS_2O_8^-$ decomposes to form reaction products in a series of steps represented by the equations:

$MS_2O_8^{n-2} + NO_2^- \overset{K_c}{\rightleftharpoons} \underset{\text{Activated complex}}{[MS_2O_8^{n-2}.NO_2^-]}$ (17)

$[MS_2O_8^{n-2}.NO_2^-] + H_2O \longrightarrow MSO_4^{n-2} + NO_3^- + SO_4^{2-} + 2H^+$ (18)

Equation (13) is the rate determining step and therefore the rate equation is :
Rate = $k_c[MS_2O_8^{n-2}][NO_2^-]$ (19)
Substituting the value of $[MS_2O_8^-]$ obtained from rearranging equation(12) in equ.14 gives:-
Rate = $K_ek_c[M^{n+}][S_2O_8^{2-}][NO_2^-]$ (20)
This equation explain the catalytic effect of the cations (i.e.Na^+ , K^+ ,Mg^{+2} , Ca^{+2} and Cu^{+2}).
Which can be reduced to:-
Rate = $k_M{}^{n+} [M^{n+}][S_2O_8^{2-}][NO_2^-]$ (21)
This is equivalent to the third term of the r.h.s. of equation (2). When i is set equal to one and when:
$k_M{}^{n+} = K_ek_c$ (22)
Equation (2) can be rewritten as:
$R_0 = k_1[S_2O_8^{2-}]_0+ k_2^0[S_2O_8^{2-}]_0 [NO_2^-]_0 + K_ek_c [M^{+n}][S_2O_8^{2-}]_0 [NO_2^-]_0$ (23)

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