Oxidation of Azide by Peroxodisulfate in Aqueous Medium

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Results on the oxidation of N_3^- by peroxodisulfate in neutral and acid media are presented. The rate of the reaction is found to be proportional to $[N_3^-]$ and $[S_2O_8^{2-}]$directly. The product of oxidation is found to be pure nitrogen. The stoichiometry of the reaction is

$$S_2O_8^{2-} + 2N_3^- = 2SO_4^{2-} + 3N_2.$$

The reaction shows positive salt effect. Thermodynamic activation parameters $\Delta H^{\ne}$ and $\Delta S^{\ne}$ have been calculated for this reaction. It is observed that H^+ ion inhibits the reaction. The mechanism is discussed in terms of the kinetic results.

Peroxodisulfate ion is a powerful two-electron oxidizing agent with a redox potential of −2.01 eV. Oxidations of both inorganic and organic substrates were reviewed by House,[1] by Wilmarth and Haim[2] and recently by Wilson[3] and by Buist.[4] The oxidations of hydroxylamine[5] and hydrazine[6] were studied by Gupta *et al.* and they reported a multi-electron-transfer from the substrate to $S_2O_8^{2-}$. The chemistry of azide has gained impetus in recent years[7,8] because of the powerful complexing properties of this ion. From a survey of the literature it appears that the oxidation of this ion by $S_2O_8^{2-}$ has not been reported so far. The reactions of this ion with triiodide ion[9,10] and carbon disulfide[11] have been studied. The present paper reports the kinetic study of the oxidation of this ion with peroxodisulfate in neutral and acid medium.

The oxidation-reduction stoichiometry of the azide-peroxodisulfate reaction in neutral medium was determined by mixing various non-stoichiometric amounts of the reactants and measuring the amount of the reactant in excess at the completion of the reaction. The results show that the redox stoichiometry of the reaction is accurately represented by

$$S_2O_8^{2-} + 2N_3^- = 2SO_4^{2-} + 3N_2. \qquad (1)$$

The product of oxidation was found to be pure nitrogen by gas chromatographic analysis in accordance with the above equation.

Experimental

Potassium peroxodisulfate (E. Merck, GR) was used without further purification. The stock solution was prepared daily and was analyzed quantitatively by cerimetry. Sodium azide (E. Merck, Germany) solution was prepared daily and was estimated by iodometry.[12] Water, deionized by passing through ion exchange resin (Permutit Mark-8) was distilled twice from alkaline permanganate in Corning glass apparatus and was stored in a stoppered polythene bottle. All solutions were prepared using this water.

Because of the high reactivity of azide ion, chemical method was not used to follow the reaction. The rate was followed by measureing the amount of gases produced from the system. The apparatus consisted of a 100 ml flask with ground glass joints. The flask was connected to a horizontal capillary tube of uniform bore of about 120 cm length, with inner diameter of ≈1.5 mm, having a mercury thread. A meter scale was attached to the tube and from the movements of the mercury thread the rate was measured.

The solution containing requisite amount of sodium perchlorate, peroxodisulfate was thermostated in the reaction vessel and was saturated with pure N_2 gas. The azide solution was thermostated separately and after the attainment of thermal equilibrium requisite amount of N_3^- solution was pipetted into the reaction vessel. The total volume of the reaction mixture was 50 ml. Powdered glass were added to avoid supersaturation. When the evolution of gas became steady, the rate was measured. It was observed that the steady state was attained within 5—10 minutes. The method was quite sensitive and the rate constant could be reproduced within 2—3%.

Results and Discussion

The plot of time *vs.* scale reading was perfectly linear (Fig. 1) and from the slope the rate d*v*/d*t* ($cm^3\,s^{-1}\,l^{-1}$) was calculated by taking the volume of the tube per cm.

N_3^- Dependence. The effect of N_3^- on rate was studied over a tenfold range of initial N_3^- concentration. The plot of log (d*v*/d*t*) *vs.* log $[N_3^-]$ shows that the rate is first order in N_3^- concentration in this range (Fig. 2).

$S_2O_8^{2-}$ Dependence. The concentration of peroxodisulfate was varied from 0.02 to 0.16 M. The plot of log (d*v*/d*t*) *vs.* log $[S_2O_8^{2-}]$ yields a slope of ≈1.0

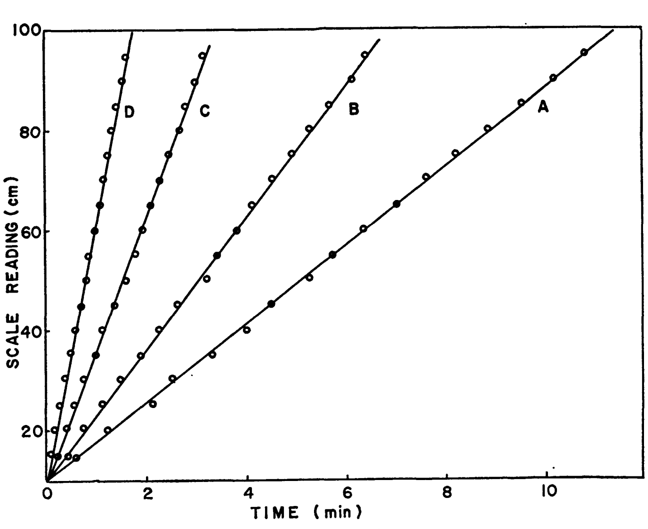

Fig. 1. The scale reading as a function of time under various initial $[N_3^-]$.
$[S_2O_8^{2-}]_0=0.04$ M; $\mu=0.92$ $t=45.0$ °C; A: 0.06 M, B: 0.10 M, C: 0.20 M, D: 0.40 M.

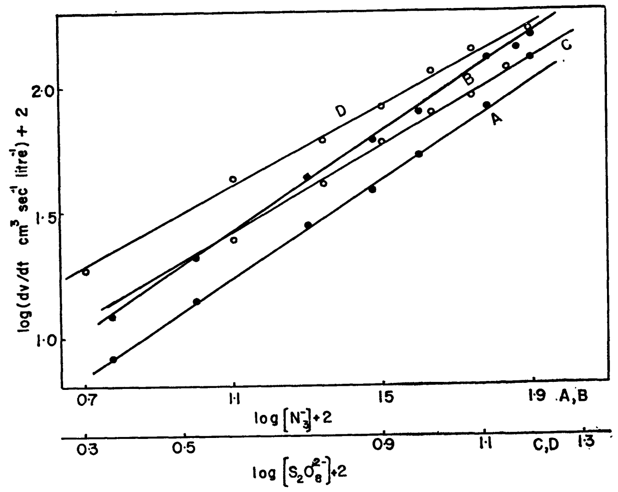

Fig. 2. Dependence of $[N_3^-]$ and $[S_2O_8^{2-}]$ on rate of the reaction.
A, B: N_3^- dependence, A: $[S_2O_8^{2-}]_0=0.04$ M; $\mu=0.92$; $t=45.0$ °C; Slope=1.0. B: $[S_2O_8^{2-}]_0=0.04$ M; $\mu=0.92$, $t=50.0$ °C; Slope=1.0. C, D: $[S_2O_8^{2-}]$ dependence. C: $[N_3^-]_0=0.20$ M; $\mu=0.72$; $t=45.0$ °C, Slope=1.15. D: $[N_3^-]_0=0.20$ M $\mu=0.92$, $t=50$ °C, Slope=1.08.

showing the first order dependence of $S_2O_8^{2-}$ (Fig. 2).

Hydrogen ion Dependence. The rate was found to decrease linearly with the addition of H^+ and almost reached to zero when the concentration of H^+ added was equal to $[N_3^-]_0$ (Fig. 3).

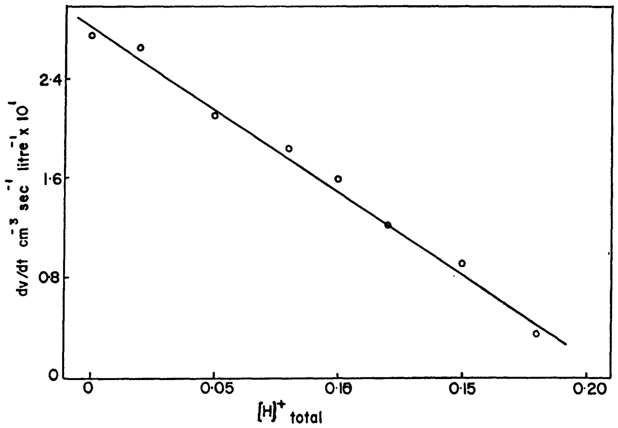

Fig. 3. Effect of H^+ on rate of the reaction. $[S_2O_8^{2-}]_0=0.04$ M; $[N_3^-]_0=0.20$ M. $\mu=0.92$; $t=45.0$ °C.

Evaluation of the Rate Constant. From the first order dependence of N_3^- and $S_2O_8^{2-}$ on rate and the stoichiometry of the reaction, the rate law could be written as

$$\frac{d[N_2]}{dt} = 3k_1[N_3^-][S_2O_8^{2-}]. \tag{2}$$

Applying the gas law Eq. 2 is modified as

$$(dv/dt)\times P/3RT = k_1[N_3^-][S_2O_8^{2-}]. \tag{3}$$

Taking $P\approx1$ atm, $T=(300\pm0.5)$ K and the initial concentrations of N_3^- and $S_2O_8^{2-}$ the absolute rate constant k_1 was calculated.

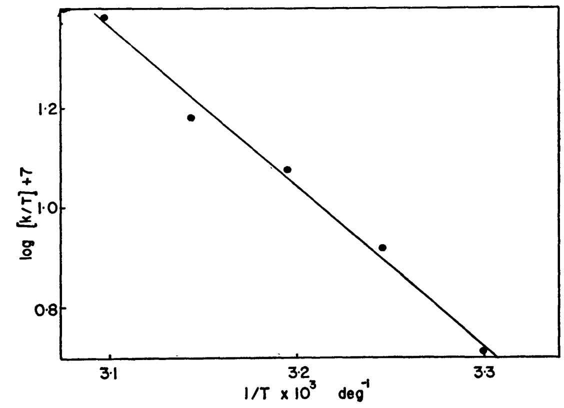

Fig. 4. Temperature dependence of k_1 between 30 and 50 °C.

Temperature Dependence. The kinetic study was made at the temperature range of 30—50°C. The plot of log (k/T) *vs.* $1/T$ was linear from which thermodynamic activation parameters were computed (Fig. 4). The values are $\Delta H^{\neq}=15.0$ kcal M^{-1} and $\Delta S^{\neq}=-25$ e.u.

Other Dependence. The rate increased with the increase in the ionic strength of the medium (Table 1). The reaction was not affected by the presence of Cu(II), Co(II), Mn(II), and Fe(III) (Table 1).

We suggest the following mechanism for the reaction in the light of the experimental results.

$$S_2O_8^{2-} + N_3^- \xrightarrow{k_1} N_3 + SO_4^{2-} + SO_4^{\cdot-} \tag{4}$$

Table 1. Rate constant of reaction of peroxodisulfate and azide ions under various conditions

$[S_2O_8^{2-}]_0=0.04$M, $[N_3^-]_0=0.20$M, $t=45.0$ °C.

Exp.	μ	$[Cu^{2+}]$ $\times 10^4$M	$[Co^{2+}]$ $\times 10^3$M	$k\times10^5$ $M^{-1}s^{-1}$
1	0.32	—	—	25.0
2	0.52	—	—	32.6
3	0.72	—	—	40.6
4	0.92	—	—	45.8
5	0.37	—	—	26.4
6	0.37	1.0	—	27.6
7	0.37	2.0	—	27.0
8	0.37	4.0	—	27.4
9	0.37	10.0	—	27.0
10	0.37	20.0	—	27.6
11	0.37	50.0	—	27.5
12	0.37	—	1.6	26.5
13	0.37	—	6.4	27.0
14	0.37	—	9.6	27.3
15	0.37	—	11.2	26.6
16	0.37	—	16.0	27.0
17	0.37	1[a]	—	27.8
18	0.37	2[a]	—	28.0
19	0.37	5[a]	—	27.5
20	0.37	10[a]	—	26.8
21	0.37	—	10[b]	27.3
22	0.37	—	20[b]	26.7
23	0.37	—	30[b]	28.0

a) $[Mn^{2+}]\times10^3$M. b) $[Fe^{3+}]\times10^5$M.

$$SO_4^{\cdot-} + N_3^- \longrightarrow N_3 + SO_4^{2-} \qquad (5)$$

$$N_3 + N_3 \longrightarrow 3N_2 \qquad (6)$$

The rate determining step is the one-electron transfer from N_3^- to $S_2O_8^{2-}$ followed by the fast consumption of SO_4^{2-} by N_3^- to form the transient species N_3 which subsequently decompose into molecular nitrogen. The reaction (6) is indeed shown13) to be very fast ($k = 1.3 \times 10^{10}\ M^{-1}\ s^{-1}$). The positive salt effect and the highly negative values of $\Delta S^{\neq}$ lend support for the above mechanism. It can be shown14) that for a bimolecular reaction between two charged species with charges Z_A and Z_B, $\Delta S^{\neq}$ would be approximately equal to $-10Z_AZ_B$. The agreement between the calculated value ($\Delta S^{\neq} \approx -20$ e.u.) and the experimental value in this investigation is reasonably good. Further, during the course of the reaction the change in the acid concentration is negligible in accordance with the above mechanism (Table 2).

Table 2. Production of acid during the reaction $\mu = 0.72$, $t = 45.0$ °C.

$[S_2O_8^{2-}]_0$	$[N_3^-]_0$	pH	
		Initial	Final
0.04	0.10	7.90	8.20
0.04	0.20	8.00	8.35
0.08	0.20	7.25	7.70
0.08	0.30	6.95	8.00
0.12	0.20	6.80	7.90

In acid medium the following steps may be included along with (3)—(6).

$$N_3^- + H^+ \overset{K_a}{\rightleftarrows} HN_3 \qquad (7)$$

$$HN_3 + S_2O_8^{2-} \xrightarrow{k_2} N_3 + HSO_4^- + SO_4^{\cdot-} \qquad (8)$$

$$SO_4^{\cdot-} + HN_3 \longrightarrow N_3 + HSO_4^- \qquad (9)$$

Surprisingly H^+ acts as an anti-catalyst for the reaction. Hydrazoic acid is a very weak acid15) ($K_a = 2.1 \times 10^{-5}$ at 20°C) with high thermal stability.16) Assuming the complete formation of HN_3 with the addition of H^+ ($[HN_3] \approx [H^+]_t$) the rate equation is given by

$$\frac{d[N_2]}{dt} = 3(k_1[N_3^-]_0 + (k_2 - k_1)[H^+]_t)[S_2O_8^{2-}], \qquad (10)$$

where $[N_3^-]_0$ represents the total concentration of azide in the solution. The value of k_2 is found to be $\approx 3.0 \times 10^{-5}\ M^{-1}\ s^{-1}$ which may be compared with k_1 ($45.8 \times 10^{-5}\ M^{-1}\ s^{-1}$). The result clearly shows that H^+ stabilizes azide ion towards $S_2O_8^{2-}$.

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