

A Kinetic Study of Electron Transfer from L-Ascorbic Acid to Sodium Perborate and Potassium Peroxy Disulphate in Aqueous Acid and Micellar Media

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ABSTRACT

Kinetics of oxidation of L-ascorbic acid (H_2A) by sodium perborate (SPB) and peroxy disulphate (PDS) have been investigated in aqueous acid and micellar media. Reaction kinetics indicated first-order dependence on both [oxidant] and $[H_2A]$. Increase in ionic strength (μ) increased reaction rate only in H_2SO_4 media. Rate of SPB oxidation of H_2A has been accelerated by acidity in HNO_3 and HCl media while a decreasing trend is observed in $HClO_4$ and H_2SO_4 media. The results are interpreted by various theories of acidity functions. Reaction rate is enhanced by the addition of added $[H_2O_2]$ indicating a H_2O_2 coordinated boron species to be active in the present system. In the absence of micelle, increase in [acid] altered the PDS— H_2A reaction rate marginally (a very small positive effect with $HClO_4$ and negative effect with H_2SO_4). Most plausible mechanisms have been proposed on the basis of experimental results. Activation parameters evaluated for specific kinetic constants are in accord with outer sphere electron transfer mechanism. In SPB— H_2A system, addition of

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anionic micelle (Sodium lauryl sulfate) increased the rate, stabilizing the cationic species in the transition state in all the acid media. Although rate of PDS oxidation of H_2A was catalyzed by TX and inhibited by SDS at critical micellar concentration (CMC) increase in [acid] (both $HClO_4$ and H_2SO_4) beyond 9.6×10^{-4} M decreased the rate of oxidation. This trend was explained due to the repulsive interaction of coanion, HA^- , and negatively charged micellar species. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Kinetic and mechanistic studies comprising electron transfer from L-ascorbic acid (H_2A) to a variety of metallic and nonmetallic reagents have been the subject of many investigations in recent times [1–4] owing to a broad spectrum of applications of L-ascorbic acid in the fields of analytical and physiological chemistry. Though the chemistry of boron and its compounds have been well documented in literature [5,6] in the past two decades, not much work appears to have been reported on the kinetics of sodium peroxoborate (SPB) oxidations in general and oxidation of L-ascorbic acid in particular. The present investigation deals with a comprehensive study of micellar catalyzed oxidation of L-ascorbic acid by peroxy compounds, SPB, and peroxy disulphate (PDS), in aqueous acid media and micellar media.

EXPERIMENTAL

Sodium peroxoborate ($NaBO_3 \cdot 4H_2O$), Peroxy disulphate ($K_2S_2O_8$), L-ascorbic acid (H_2A), H_2O_2 , sodium lauryl sulphate, Triton-X 100, and cetyl trimethyl ammonium bromide have been procured from Fluka-AG, Switzerland. Acetic acid was refluxed over Cr_2O_3 and acetic anhydride for about 6 h and distilled twice before use according to literature procedures [7]. All the other chemicals employed are of E-merck (GR) samples. SPB solution has been estimated according to literature procedures [8]. Stock solutions required for each set of experiments have always been prepared fresh and stored in amber colored bottles in a refrigerator. Requisite amounts of each reagent are pipetted out into reaction flasks and the contents have been thermally equilibrated at a desired temperature in a constant temperature bath of $\pm 0.1^\circ C$ accuracy. Reaction is initiated by adding H_2A as the last component and the rate of disappearance of $[H_2A]$ has been followed titrimetrically by estimating the unreacted $[H_2A]$ at regular time intervals using standard I_2 at starch end point [9]. The results thus obtained have been randomly confirmed by estimating dehydro ascorbic acid [A] spectrophotometrically according to the method of

Roe [10,11]. The values are in good agreement with each other within experimental limits of $\pm 3\%$ error.

Addition of olefinic monomers such as deaerated acrylonitrile or freshly prepared 10% acrylamide to the reaction mixture indicated the vinyl polymerization of acrylamide and/or acrylonitrile suggesting the formation of free radical intermediates during the course of reaction. Blank experiments, from which either oxidant (SPB or PDS) or H_2A were excluded, yield no detectable polymer.

RESULTS AND DISCUSSION

Kinetics of the SPB— H_2A Reaction

Stoichiometry of the reaction revealed that one mol of ascorbic acid consumed one mol of sodium peroxoborate to yield dehydro ascorbic acid as an oxidation product in all the acid media.

Under pseudo-first-order conditions viz. $[H_2A] \ll [SPB]$, the order in $[H_2A]$ has been found to be unity in all the acid media at constant acidity, ionic strength (μ), and temperature. This can be readily seen from the plot of $\log ([H_2A]_0/[H_2A]_t)$ vs. time, which is linear passing through origin (Fig. 1).

Under the conditions $[SPB] = [H_2A]$, plot of $[H_2A]^{-1}$ vs. time has been found to be linear with a definite intercept on $[H_2A]_t^{-1}$ -axis thus exhibiting overall second-order in SPB— H_2A system at constant acidity and μ . Similar observations have been recorded in all the acid media (Fig. 2).

Effect of $[NH_4BO_2]$: A variation in $[NH_4BO_2]$, reduced species of peroxoborate, over a ten fold range (0.01 to 0.10 mol dm^{-3}) did not alter the second-order rate constant to any considerable extent.

Effect of [salt]: A variation in $[NaClO_4]$ (0.010 to 0.100 mol dm^{-3}) increased the rate of oxidation marginally in $HClO_4$ medium. A similar variation of $[KHSO_4]$ (0.010 to 0.100 mol dm^{-3}) increased the second-order rate constant from 0.560 to 3.60 dm^3 mol $^{-1}$ s $^{-1}$ in sulphuric acid medium. However, such studies (KNO_3 and $NaClO_4$ in HNO_3 medium and KCl and $NaClO_4$ in HCl medium) in HNO_3 and HCl media revealed that rate is independent on [salt].

Effect of [acid] and acidity functions: At constant ionic strength (μ) an increase in acidity decreases the rate of oxidation in $HClO_4$ and H_2SO_4 media

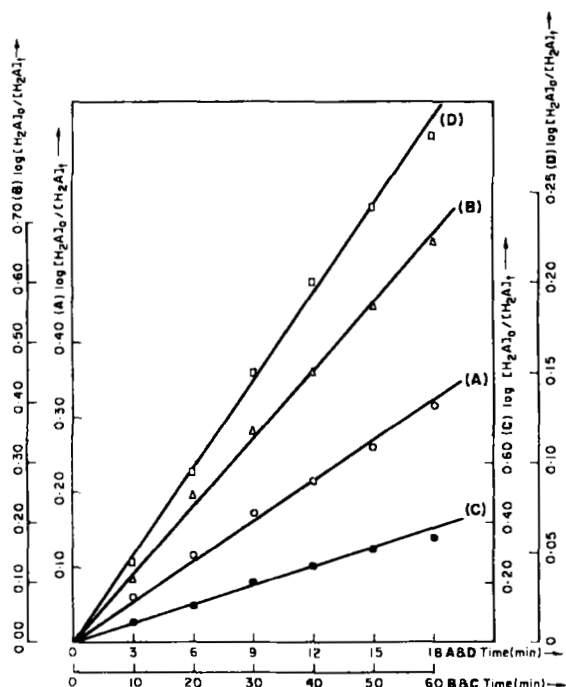


Figure 1 Plots of $\log([H_2A]_0/[H_2A]_t)$ versus time (min). 10^2 [SPB] = 2.00 mol dm^{-3} , $\mu = 0.200 \text{ mol dm}^{-3}$, Temp. = 313 K . (A) $10^3[H_2A] = 2.00 \text{ mol dm}^{-3}$, $[HClO_4] = 0.100 \text{ mol dm}^{-3}$. (B) $10^3[H_2A] = 4.00 \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.100 \text{ mol dm}^{-3}$. (C) $10^3[H_2A] = 4.00 \text{ mol dm}^{-3}$, $[HNO_3] = 0.100 \text{ mol dm}^{-3}$. (D) $10^3[H_2A] = 4.00 \text{ mol dm}^{-3}$, $[HCl] = 0.100 \text{ mol dm}^{-3}$.

but increases with increasing concentration of HCl and HNO_3 (Table I). This observation may indicate that the nature of predominating reactive species differs from one acid to the other. However, one cannot rule out the possibility of oxidation of H_2A by mineral acid [12] because all the acids except HCl are oxidizing agents. In order to know whether the acids employed are competing with SPB in the oxidation, the reactions are conducted separately in the absence of SPB under otherwise similar conditions. It was observed that rate of oxidation was almost negligible in the absence of SPB.

In order to gain further insight into the mechanistic aspects and role of water molecule participation in the slow step, the second-order rate constants (k'') presented in Table I were cast into various theories of acidity functions [13–16].

Least-square analysis of Zucker–Hammett's plots viz., $\log k''$ vs. $\log[\text{Acid}]$, $H\nu$ were linear with the slopes equal to m and $m^\#$, respectively. The values of " m " were 0.50, 0.48, -0.30 , and -0.28 in HNO_3 , HCl, $HClO_4$, and H_2SO_4 , respectively. In the same sequence the values of " $m^\#$ " were -0.40 , -0.36 ,

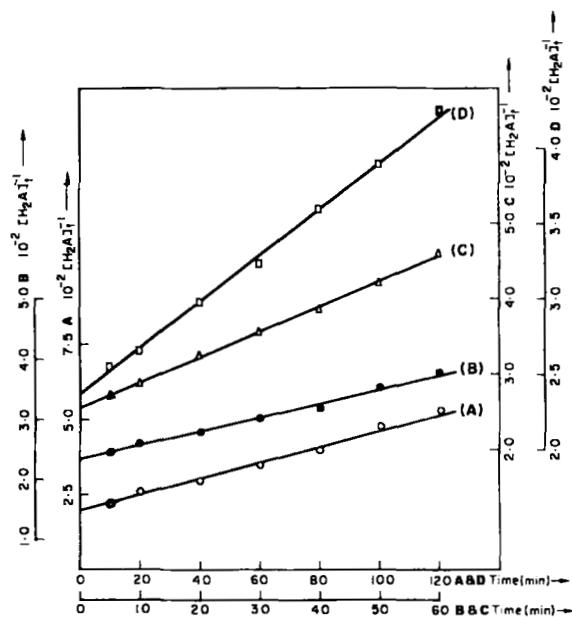


Figure 2 Plots of $[H_2A]_t^{-1}$ versus time (min). (A) $HClO_4$, (B) H_2SO_4 , (C) HNO_3 , (D) HCl; 10^3 [SPB] = 10^3 $[H_2A] = 4.00 \text{ mol dm}^{-3}$, $[\text{Acid}] = 0.100 \text{ mol dm}^{-3}$, $\mu = 0.200 \text{ mol dm}^{-3}$, Temp. = 323 K .

0.31, and 0.35. The slopes (m and $m^\#$) are less than unity in all the cases, which may indicate the participation of water molecule in the rate limiting step.

To confirm the role of water molecule in slow step, the data were treated by Bunnett's approach. Bunnett's plots of $(\log k'' + H\nu)$ and $(\log k'' + \log[\text{Acid}])$ vs. $\log a_{H_2O}$ were linear with the slopes equal to ω and $\omega^\#$, respectively. The values of ' ω ' were, viz., -50.6 , -43.0 , -127 , and -127 in HNO_3 , HCl, $HClO_4$, and H_2SO_4 , respectively. The values of ' $\omega^\#$ ' were also very high in the same sequence: 148, 155, 70.0, and 72.0. Owing to such unassumingly high values of ω and $\omega^\#$, nothing much could be concluded about role of water molecule.

The data were further treated with Bunnett–Olson's hypothesis [13–16]. The plots of $(\log k'' + H\nu)$ and $(\log k'')$ vs. $(H\nu + \log[\text{Acid}])$ were found to be linear with the slopes of ϕ and $\phi^\#$, respectively. The ϕ values in all the cases were less than one (0.254, 0.225, 0.644, and 0.606 in HNO_3 , HCl, $HClO_4$, and H_2SO_4 , respectively). However, the $\phi^\#$ values were 0.239, 0.275, -0.154 , and -0.158 in HNO_3 , HCl, $HClO_4$, and H_2SO_4 , respectively. The positive $\phi^\#$ values in HNO_3 and HCl could probably substantiate the role of water molecule as a proton abstracting agent in the slow step. The negative values in $HClO_4$ and H_2SO_4 media probably depict the noninvolvement of molecule in the slow step.

Table I Second-Order Rate Constants for SPB—H₂A System at 313 K 10^3 [SPB] = 10^3 [H₂A] = 4.00 mol dm⁻³ and μ = 0.200 mol dm⁻³

[H ⁺]/ mol dm ⁻³	10^3 [H ₂ O ₂]/ mol dm ⁻³	HOAC (% v/v)	Temp (K)	Second-Order Rate Constant (k'')/dm ³ mol ⁻¹ min ⁻¹			
				HClO ₄	H ₂ SO ₄	HNO ₃	HCl
0.010	—	—	313	2.50	5.60	1.22	0.667
0.020	—	—	313	1.60	3.30	1.28	0.729
0.050	—	—	313	1.05	2.64	1.54	0.906
0.100	—	—	313	0.790	2.10	1.94	1.10
0.150	—	—	313	0.699	1.86	2.31	1.35
0.200	—	—	313	0.640	1.72	2.70	1.60
0.100	—	4.00	313	—	0.857	1.68	0.857
0.100	—	10.0 (72.6)	313	0.970	1.00	1.70	0.947
0.100	—	20.0 (65.2)	313	1.15	1.08	1.85	0.909
0.100	—	40.0 (50.4)	313	1.70	1.33	2.00	1.06
0.100	—	60.0 (35.6)	313	2.82	2.70	4.67	1.75
0.100	—	80.0 (20.8)	313	—	6.67	10.0	2.05
0.010	2.60	—	297	0.790	0.880	0.920	1.04
0.010	5.20	—	297	2.48	2.16	2.83	2.71
0.010	7.80	—	297	4.23	4.80	5.18	4.56

Values in the parenthesis indicate dielectric constant (D) values.

Added H₂O₂ enhanced the rate of reaction to a greater significance in all the acid media studied (Table I).

In all the four acids, an increase in the rate of oxidation with an increase in the composition of acetic acid or a decrease in the dielectric constant (D) of the medium has been recorded (Table I).

In all the acid media studied, addition of sodium Dodecyl sulphate (SDS) increased the rate of reaction up to 0.003 mol dm⁻³ (slightly above critical micellar concentration —CMC) and decreases gradually (Table II). However, such studies in the presence of cetyl trimethylammonium bromide (CTAB) did not show any significant increase or decrease as indicated by the data compiled in Table III.

At constant ionic strength (μ) and temperature, second-order rate constants (k'') increase with decreasing acidity in HClO₄ and H₂SO₄ media. The plots of k'' vs. [acid]⁻¹ have been found to be linear with positive gradient and definite intercept on k'' -axis, suggesting an empirical rate law to be applicable in perchloric and sulphuric acid media [17]

$$\frac{-d[\text{H}_2\text{A}]}{dt} = \frac{-d[\text{SPB}]}{dt} = \left(a + b[\text{H}^+]^{-1} \right) [\text{SPB}] [\text{H}_2\text{A}] \quad (1)$$

the decelerating effect of [H⁺] on reaction rate, further, suggests the participation of anion in the rate limiting step.

Reaction kinetics in HNO₃ and HCl media indicated first-order dependence in [SPB] and [H₂A] at constant [acid] and μ . Reaction rate is independent of [salt]. Over a wide variation in acidity (0.010 to 0.20 mol dm⁻³) second-order rate constant exhibited an accelerating effect with a trend: HNO₃ > HCl. An

Table II Effect of [SDS] on SPB—H₂A System in Various Acid Media 10^3 [SPB] = 10^3 [H₂A] = 4.00 mol dm⁻³; [H⁺] = 0.01 mol dm⁻³; μ = 0.200 mol dm⁻³; and Temp = 298 K

10^3 [SDS]/ mol dm ⁻³	k_ϕ /dm ³ mol ⁻¹ min ⁻¹			
	HClO ₄	H ₂ SO ₄	HNO ₃	HCl
0.00	0.400	0.330	0.200	0.428
1.00	0.630	0.615	0.350	0.575
2.00	0.830	0.914	0.542	0.714
4.00	0.925	1.290	0.675	0.960
6.00	0.950	1.490	0.750	1.120
8.00	0.965	1.630	0.800	1.220
10.00	0.960	1.670	0.820	1.280
12.00	0.925	1.660	0.795	1.270
16.00	0.590	1.420	0.575	0.790
20.00	0.240	0.310	0.275	0.300

Table III Effect of [CTAB] on SPB—H₂A System in Various Acid Media $10^3[\text{SPB}] = 10^3[\text{H}_2\text{A}] = 4.00 \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$; $\mu = 0.200 \text{ mol dm}^{-3}$; and Temp = 298 K

$10^3[\text{CTAB}]/$ mol dm^{-3}	$k_{\phi}/\text{dm}^3\text{mol}^{-1}\text{min}^{-1}$			
	HClO ₄	H ₂ SO ₄	HNO ₃	HCl
0.00	0.400	0.330	0.200	0.428
0.50	0.330	0.387	0.200	0.410
1.00	0.333	0.400	0.200	0.425
2.00	0.336	0.407	0.225	0.430
3.00	0.345	0.410	0.240	0.432
4.00	0.360	0.415	0.265	0.435
5.00	0.366	0.422	0.288	0.444
6.00	0.370	0.426	0.294	0.451

empirical rate law which obeys the reaction kinetics [17] can be given as

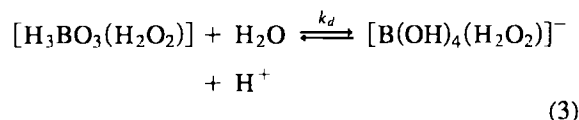
$$\begin{aligned} \frac{-d[\text{H}_2\text{A}]}{dt} &= \frac{-d[\text{SPB}]}{dt} \\ &= \{a' + b'[\text{H}^+]\}[\text{SPB}][\text{H}_2\text{A}] \quad (2) \\ &= k''[\text{SPB}][\text{H}_2\text{A}] \end{aligned}$$

Reactive Species and Mechanism of Oxidation

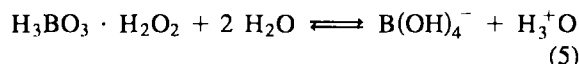
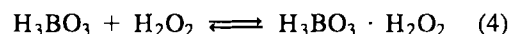
In a redox system, the nature of the oxidizing as well as reducing species is important in order to envisage the mechanistic pathway. Ascorbic acid (H₂A) and dehydro ascorbic acid(A/) can be viewed as antagonists since their activities follow opposing trends. According to the dissociation equilibria in aqueous solutions [1–4], besides the neutral H₂A itself, ascorbic acid exists as ascorbate ions (HA⁻, A²⁻, the monovalent and divalent ionic species), ascorbate radical (HA[•]), ascorbate radical ions (HA^{-•} and A^{-•} monohydro and dehydro ascorbate radical ions) and ascorbic acid-ascorbate complex are reported as the intermediate species in literature. Finholt and co-workers [11] proposed the possibility of a complex formation between H₂A and HA⁻ to give H₂A.HA⁻, while studying the aerobic oxidation of H₂A under the conditions, pH = 3.52–7.22, ionic strength (μ) = 0.40, and temperature = 27°C. On the basis of dissociation equilibria under experimental acid conditions (> = 0.01M), undissociated H₂A species only appear to be important in the present study.

From X-ray crystallographic studies, the structure of sodium perborate is established as Na₂X₆H₂O [18]. The structural elucidation exhibits two Na⁺ ions, six water molecules, and the centrosymmetric cyclic anion, x²⁻ (where x²⁻ = [B₂(O₂)₂(OH)₄]²⁻). In the anion boron atoms are joined by two per-

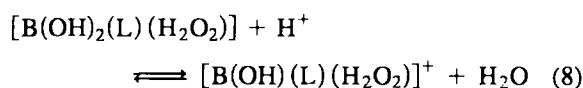
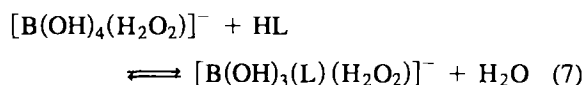
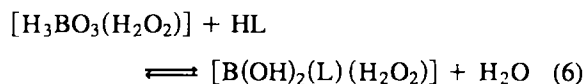
oxobridges and their tetrahedral coordination is completed by terminal OH groups. However, the constitution of solutions of perborate is rather difficult but interesting problem [18–20]. It has earlier been mentioned that the so-called sodium perborate is not peroxoborate but borate peroxy hydrate, H₂O₂ acquiring stronger electrophilicity by the coordination with the boric acid, which acts as Lewis acid rather than protic acid. Extensive conductometric and cryoscopic investigations [20] on borate-H₂O₂ systems revealed that H₂O₂ is associated with borate thus supporting the above contention. It is also interesting to note [20] that perborate exists as monomer, in a solution of below 0.05 mol dm⁻³ concentration in the forms of SPB and SPB ([B(OH)₄(H₂O₂)]⁻ = SPB⁻ and/or [H₃BO₃(H₂O₂)] = SPB) according to the following dissociation equilibrium.



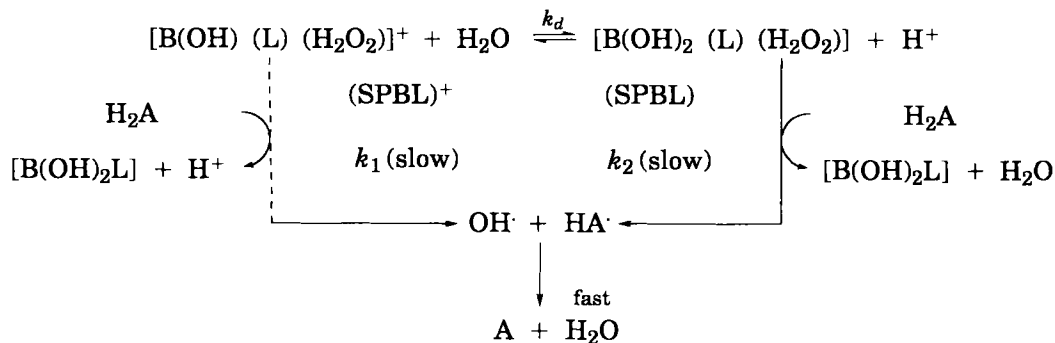
Dissociation constant (K_d) value of step (3) was found to be in the range of 10⁻⁸ [19,20]. It is, therefore, reasonable to consider only undissociated form of sodium perborate (SPB) as the active oxidizing species even in very low acidities. Further, the observed enhancement in the rate of oxidation with added H₂O₂ indicate that H₂O₂ coordinated boron moiety is the reactive species which can be explained according [19] to the following equilibria



In addition to the above features, [H₃BO₃(H₂O₂)] or [B(OH)₄(H₂O₂)]⁻ may also combine with HSO₄⁻ in H₂SO₄ to form a sulphate species or similar type of other anionic species in the presence of mineral acid (HL where L = HSO₄⁻, NO₃⁻, Cl⁻, and ClO₄⁻) according to the following equilibria.



These contentions can be supported from acidity and salt effects on the rate of oxidation.



Scheme I

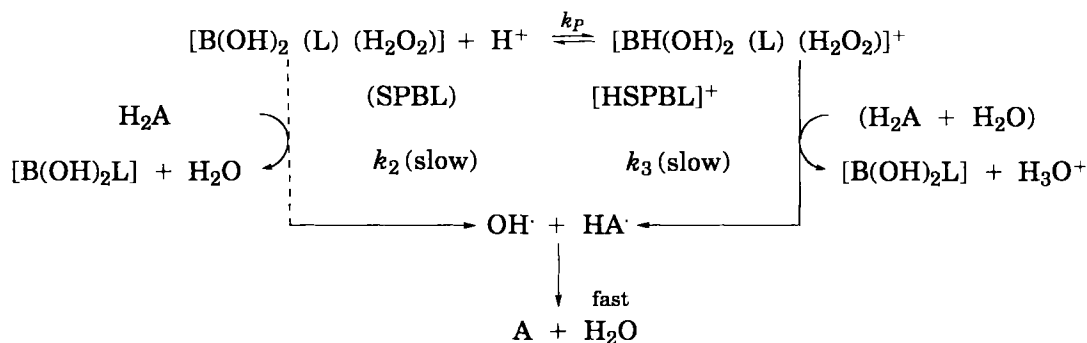
In all the four acid media, an increase in rate with a decrease in *D* of the medium (a plot of $\log k$ vs. D^{-1} with a positive slope) suggests the involvement of cation-dipoles interaction in the slow step(s) according Laidler–Eyring [21] and Amis [22] theories by ruling out the participation of anion-dipole and dipole-dipole. The above discussion, therefore, substantiates the participation of $[\text{B(OH)L(H}_2\text{O}_2)]^+$ and H_2A , as reactive species in the rate limiting step(s).

Alternatively, the rate enhancement with increase in the composition of acetic acid can also be explained due to the generation of more active oxidizing species such as peracetic acid due to the oxidation of acetic acid by sodium perborate in aqueous acid media [19].

On the basis of the observed kinetic features and foregoing discussion coupled with the presence of free radicals a plausible mechanism of oxidation could be presented as in Scheme I. This mechanism depicts that water molecule is not involved in the slow step(s) which could be supported from the negative slopes ($\phi^\ddagger = -0.158$ and -0.154 in HClO_4 and H_2SO_4 media, respectively) obtained from the linear plot of Bunnett–Olsen’s hypothesis.

At constant ionic strength (μ) the rate law for the above mechanism comes out as,

$$-\frac{d[\text{H}_2\text{A}]}{dt} = -\frac{d[\text{SPB}]}{dt} = k''[\text{SPB}][\text{H}_2\text{A}] \quad (9)$$

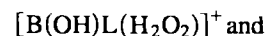


Scheme II

where

$$k'' = \{(k_1\text{CH}^+ + k_2K_d)/(\text{CH}^+ + K_d)\}$$

K_d = the dissociation constant of



$\text{L} = \text{HSO}_4^-$ and ClO_4^- .

when $[\text{H}^+] \gg K_d$ and both (SPBL) well (SPBL)⁺ are reactive

$$k'' = k_1 + k_2K_d[\text{H}^+]^{-1}$$

consequently the rate law can be written as.

$$-\frac{d[\text{H}_2\text{A}]}{dt} = (k_1 + k_2K_d[\text{H}^+]^{-1}) [\text{SPB}][\text{H}_2\text{A}] \quad (10)$$

The linearity of first-order plots and the absence of $[\text{NH}_4\text{BO}_2]$ effect on reaction rate coupled with decelerating effect of $[\text{H}^+]$ support the validity of rate law in HClO_4 and H_2SO_4 media. This rate law is in accordance with the experimental rate law (1). The comparison of rate eq. (10) with empirical rate law (1) shows that $a = k_1$ and $b = k_2K_d$.

The plot of (k'') as a function of $[\text{H}^+]^{-1}$ resulted in a straight line with positive slope and intercept on (k'')-axis. From intercept and slope 'a' and 'b'

can be determined. Alternatively rearrangement of expression for k'' in eq. (10)

$$k''[\text{H}^+] = k_1[\text{H}^+] + k_2K_d \quad (11)$$

The plot of $k''[\text{H}^+]$ as a function of $[\text{H}^+]$ has also been found to be linear with positive slope and intercept (Fig. 3(a) and (b)). From the slope value specific rate constant k_1 has been determined. Due to the complexity k_2 could not be evaluated precisely. However, the composite value of $K_d k_2$ have been evaluated and compiled in Table IV. Activation parameters involving k_1 have been evaluated from the theory of absolute reaction rates [21] and are presented in Table IV.

Observed kinetic features coupled with the acid catalysis due to HNO_3 and HCl and the positive values of slopes (ϕ^\ddagger) observed from the plots of Bunnett-Olsen's hypothesis of acidity functions substantiate the protonation of SPBL and the participation of water molecule in the rate determining step as shown in Scheme II.

For Scheme II, the rate law comes out as,

$$-\frac{d[\text{H}_2\text{A}]}{dt} = -\frac{d[\text{SPB}]}{dt} = k''[\text{SPB}][\text{H}_2\text{A}] \quad (12)$$

where

$$k'' = \{(k_2 + k_3K_p[\text{H}^+])/(1 + K_p[\text{H}^+])\}[\text{SPB}][\text{H}_2\text{A}]$$

K_p = the protonation constant and

$L = \text{NO}_3^-$ or Cl^- .

If an assumption is made in eq. (12) that $K_p[\text{H}^+] \ll 1$ in HCl and HNO_3 media, the equation reduces to

$$k'' = k_2 + k_3K_p[\text{H}^+] \quad (13)$$

Expression (13) resembles k'' of eq. (2) thus showing the validity of the proposed mechanism in HNO_3 and HCl media. According to this expression a plot of k'' vs. $[\text{H}^+]$ should be a straight line with positive slope (b') and definite intercept (a') on k'' -axis

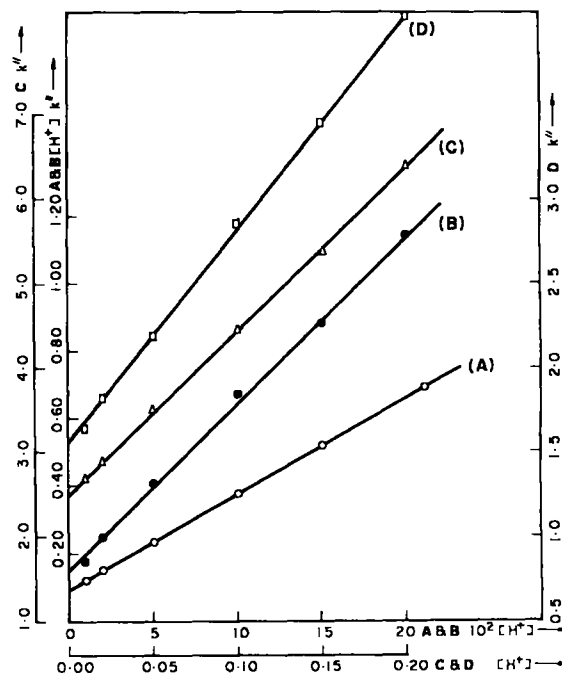


Figure 3 (A & B) Plots of $k''[\text{H}^+]$ versus $[\text{H}^+]$. (A) HClO_4 , (B) H_2SO_4 medium. $10^3[\text{SPB}] = 10^3[\text{H}_2\text{A}] = 4.00 \text{ mol dm}^{-3}$, $\mu = 0.200 \text{ mol dm}^{-3}$, Temp. = 333 K. (C & D) plots of k'' versus $[\text{H}^+]$. (C) HNO_3 , (D) HCl . $10^3[\text{SPB}] = 10^3[\text{H}_2\text{A}] = 4.00 \text{ mol dm}^{-3}$, $\mu = 0.200 \text{ mol dm}^{-3}$, Temp. = 333 K.

(where $a' = k_2$ and $b' = k_3K_p$). Such plots have been realized in HNO_3 and HCl media of the present study (Fig. 3 (c) and (d) indicating the correctness of proposed mechanism. The values of k_1 and k_2 and corresponding activation parameters have been represented in Table IV.

Assumptions made in Scheme I and Scheme II appeared to be justified owing to the fact that the obtained rate equations (10) and (12) are in accordance with the observed kinetic results of empirical rate expressions (1) and (2), respectively. The foregoing results probably indicate that mechanism changes with a change in the nature of ligand environment of the mineral acid used. Activation enthalpies obtained

Table IV Specific Rate Constants and Activation Parameters

Parameter	Temp (K)	Reaction Medium			
		HClO_4	H_2SO_4	HNO_3	HCl
k_i ($\text{dm}^3\text{mol}^{-1}\text{min}^{-1}$)	313	0.560	1.58	1.15	0.650
ΔH^\ddagger (kJ mol^{-1})		85.1	27.1	23.9	34.3
ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$)		79.4	-101	-110	-81.60
$(K_d k_2)$	313	0.020	0.043	-	-
$k_3 K_p$	313	-	-	0.125	0.200

^aRate constant (k_i) represents k_1 in the case of HClO_4 and H_2SO_4 ; k_2 in the case of HNO_3 and HCl media.

are in the range of redox reactions according to literature reports [23]. Entropies of activation (ΔS^\ddagger) show that transition state is more solvated in all the acid media excepting perchloric acid. This trend may be attributed to a relatively less hinderance of ClO_4^- which may facilitate a greater interaction between the reactive species in the transition state.

Formation of free radical intermediates such as HA^\cdot and OH^\cdot in the proposed mechanism has been invoked by earlier workers [1,24] in the oxidation of ascorbic acid by peroxy disulphate and metal ion catalyzed H_2O_2 systems. Since SPB is also a peroxy compound formation of OH^\cdot radical may be reasonable.

From the data compiled in Table IV it could be seen that gross experimental second-order rate constants (k'') are in the order: $\text{H}_2\text{SO}_4 > \text{HClO}_4 > \text{HNO}_3 > \text{HCl}$. However the values of k_2K_d appear to follow the order: $\text{H}_2\text{SO}_4(23.2) < \text{HClO}_4(50.2)$ which is by and large according to the electron withdrawing nature of the anion of oxidizing species. The values of k_3K_p indicate by and large a similar order, $\text{HCl} > \text{HNO}_3$, which is in accordance with the electron withdrawing nature of anion of oxidizing species.

MECHANISM OF OXIDATION IN PDS— H_2A SYSTEM

PDS— H_2A reaction indicated second-order kinetics with a first-order dependence on each of the reactants [PDS] and $[\text{H}_2\text{A}]$ in HClO_4 as well as H_2SO_4 media, which were realized from the plots of $[\text{PDS}]^{-1}$ vs. time and $\log(a/a-x)$ vs. time (figures are not given), respectively. Variation of $[\text{K}_2\text{SO}_4]$ or $[\text{KCl}]$ from 0.001 to 0.05 mol dm^{-3} did not alter the second-order rate constant to any significant extent either in sulphuric or perchloric acid media. An increase in $[\text{H}_2\text{SO}_4]$ indicated a slight decrease in the second-order rate constant when $[\text{H}_2\text{SO}_4]$ is increased by 16 fold. A similar study in HClO_4 medium hardly affected the rate of constant (Table V).

Although the rate of oxidation was slightly decreased by acidity in sulphuric acid medium the acid concentration used in the present study is far greater than the dissociation constant (K_1) of H_2A . Under these conditions, distribution studies revealed that ascorbic acid mainly exists as undissociated H_2A (>90%). Hence, undissociated form of H_2A could be reasonably assumed as the main reactive species. If ion-ion type of reaction could be proposed as rate determining step, according to Ingold rule rate of oxidation should have been remarkably enhanced in the solvent of low dielectric constant [25]. However, the rate of oxidation has been found to be moderately faster in the solvent of low dielectric constant (Table VI). Since the plots of $\log k$ vs. $(D)^{-1}$ (figures not shown) were linear, the results probably point out the participation of cation and dipole according to Amis theory. If this were to be acceptable, rate of the reaction should have been accelerated with an increase in the ion power of the solution. However, the rate is hardly influenced by an increase in [Salt]. Alternatively, the observed results could be better explained by Laidler–Eyring theory [21] which is applicable for cation-dipole as well as anion-dipole type reaction as rate limiting step.

On the basis of foregoing kinetic features, two possible mechanisms could be proposed by considering either the reaction between $\text{S}_2\text{O}_8^{2-}$ and H_2A in the rate limiting step or the reaction between $\text{SO}_4^{\cdot-}$ and H_2A in the rate limiting step.

It has earlier been mentioned that in peroxydisulphate symmetrically decomposes to give two sulphate radical ions [26,27]. The radical ion ($\text{SO}_4^{\cdot-}$) thus produced has been assumed to react with H_2A in the rate limiting step, to give products, according to the following reaction sequence.

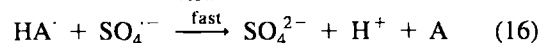
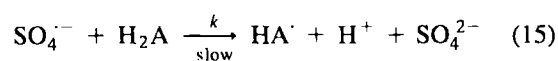
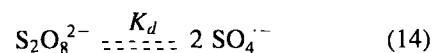


Table V Effect of Variation of [Acid] on PDS— H_2A Reaction [PDS] = 0.02 mol dm^{-3} ; $[\text{H}_2\text{A}] = 0.002 \text{ mol dm}^{-3}$; and Temp = 298 K

$10^4[\text{Acid}]$ mol dm^{-3}	$10^4 k' [\text{HClO}_4] (\text{min}^{-1})$			$10^4 k' [\text{H}_2\text{SO}_4] (\text{min}^{-1})$		
	Without Micell	At CMC of SDS	At CMC of Triton-X	Without Micell	At CMC of SDS	At CMC Triton-X
4.8	1.97	2.29	2.13	2.35	2.04	1.64
9.6	2.12	2.20	2.00	2.27	1.94	1.52
19.2	2.19	2.08	1.84	2.11	1.82	1.40
38.4	2.21	1.99	1.78	1.92	1.70	1.28
67.2	2.23	1.95	1.63	1.75	1.56	1.15

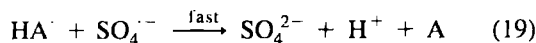
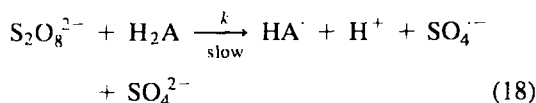
Table VI Effect of Solvent [MeOH] on PDS—H₂A Reaction [PDS] = 0.02 mol dm⁻³; [H₂A] = 0.002 mol dm⁻³; and Temp = 298 K 10³[H₂SO₄] = 10³[HClO₄] = 2.4 mol dm⁻³

MeOH (%v/v)	10 ⁴ k' (HClO ₄ Medium) (min ⁻¹)			10 ⁴ k' (H ₂ SO ₄ Medium) (min ⁻¹)		
	Without Micell	At CMC of SDS	At CMC of Triton-X	Without Micell	At CMC of SDS	At CMC Triton-X
4	1.82	2.46	2.44	1.90	2.39	1.97
8	1.99	2.55	2.62	1.96	2.44	2.04
12	2.08	2.62	2.76	2.02	2.58	2.12
16	2.18	2.71	2.83	2.07	2.73	2.26
28	2.26	2.88	2.95	2.10	2.80	2.32

The rate law according to the above mechanism could be written as

$$\frac{d[\text{PDS}]}{dt} = k_x [\text{S}_2\text{O}_8^{2-}]^{1/2} [\text{H}_2\text{A}] \quad (17)$$

where $k_x = k K_d^{1/2}$. This rate law shows first-order dependence on [H₂A] and half-order (0.5) dependence on [S₂O₈²⁻], which is not in accordance with the observed kinetics. It is, therefore, thought to consider the ion-dipole reaction between S₂O₈²⁻ and H₂A as rate limiting step. The mechanistic path has been shown in the following steps.



Rate law, for this mechanism, comes out as,

$$-\frac{d[\text{PDS}]}{dt} = k [\text{S}_2\text{O}_8^{2-}] [\text{H}_2\text{A}] \quad (20)$$

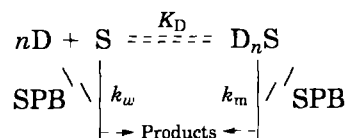
This shows an overall second-order kinetics with a first-order dependence on [S₂O₈²⁻] and [H₂A], which is in accordance with the observed reaction kinetics and keeping with the proposed mechanism. Formation of radical species such as HA[·] and SO₄^{·-} could be supported on the basis of observed vinyl polymerization of added acrylo nitrile monomer to the reaction mixture. A perusal of the k''-values shows that the reactivity is in accordance with a decrease in the electron withdrawing nature of anion ClO₄⁻ < HSO₄⁻.

MECHANISM OF OXIDATION OF H₂A IN THE PRESENCE OF ANIONIC MICELLES (SDS):

From the second-order rate constants data presented in Tables II and III for SPB—H₂A, VII and VIII for PDS—H₂A systems, respectively, the following observations have been recorded: (i) In all the acid media (HCl, HClO₄, HNO₃, and H₂SO₄) SDS indicated

catalytic effect in SPB—H₂A system (Table II and III). However, the plots of k_φ vs. C_D [surfactant] indicated rate maxima nearly in the vicinity of critical micellar concentration (CMC) of SDS and above CMC, k_φ-values gradually decreased (Fig. 4) and (ii) In H₂SO₄ and HClO₄ media k_φ vs. C_D profile indicated that SDS inhibits the rate of oxidation (Table VII) of H₂A by PDS.

Recently, Piszkievicz adopted cooperativity model on the basis of a mathematical model developed by Bruce et al. According to this model substrate(s) combines with 'n' molecules of detergent (D) to form a catalytic micelle D_nS which may then react to give products [28,29].



Rate law for this model comes out as,

$$k_\phi = \frac{k_m [\text{D}]^n + k_w K_D}{K_D + [\text{D}]^n}$$

Subtracting k_φ from both the sides and rearranging further

$$\frac{(k_\phi - k_w)}{(k_m - k_\phi)} = \frac{[\text{D}]^n}{K_D} \quad (22)$$

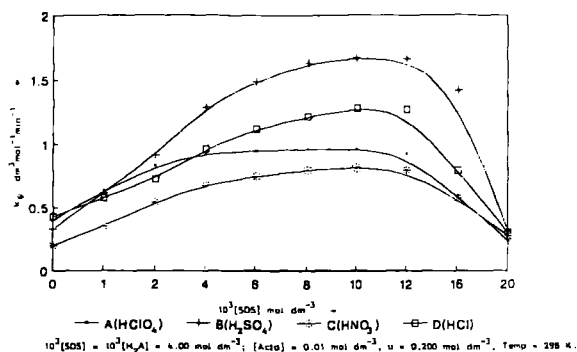


Figure 4 Plots of k_φ versus [SDS].

Table VII Effect of [SDS] on PDS—H₂A System in Various Acid Media [PDS] = 0.02 mol dm⁻³; [H₂A] = 0.002 mol dm⁻³; and 10³[H₂SO₄] = 10³[HClO₄] = 2.4 mol dm⁻³

10 ³ [SDS] (mol dm ⁻³)	10 ⁴ k _φ (min ⁻¹)			
	H ₂ SO ₄ Medium		HClO ₄ Medium	
	298 K	308 K	298 K	308 K
2.00	2.63	5.85	3.05	5.84
4.00	2.54	5.71	3.01	4.56
6.00	2.44	5.59	2.98	4.28
8.00	2.35	5.50	2.97	4.20
10.00	2.27	5.38	2.94	4.04
12.00	2.20	5.28	2.92	3.96
16.00	2.10	5.11	2.81	3.88
20.00	2.02	4.96	2.58	3.84
24.00	1.96	4.83	2.34	3.76
28.00	1.90	4.70	2.12	3.72
32.00	1.85	4.60	1.98	3.68
36.00	1.81	4.51	1.88	3.60

Taking logarithms on both the sides

$$\log \left\{ \frac{k_{\phi} - k_w}{k_m - k_{\phi}} \right\} = n \log [D] - \log K_D \quad (21)$$

When $K = 1/K_D$, the above equation takes the form,

$$\log \left\{ \frac{k_{\phi} - k_w}{k_m - k_{\phi}} \right\} = n \log [D] + \log K$$

The plots of $\log\{(k_{\phi} - k_w)/(k_m - k_{\phi})\}$ vs. $\log [D]$ should be straight line with a positive slope and an intercept. Such plots have been realized in SDS catalysis of the present study (Fig. 5). The binding constant values ($\log K$) obtained for SPB—H₂A system are 3.27, 6.70, 1.18, and 3.58 in HClO₄, H₂SO₄, HNO₃, and HCl media, respectively. Inhibition due to sodium dodecyl sulphate (SDS) in PDS—H₂A system has been explained according to the micellar model proposed by Menger et al. and Bunton et al. [28]

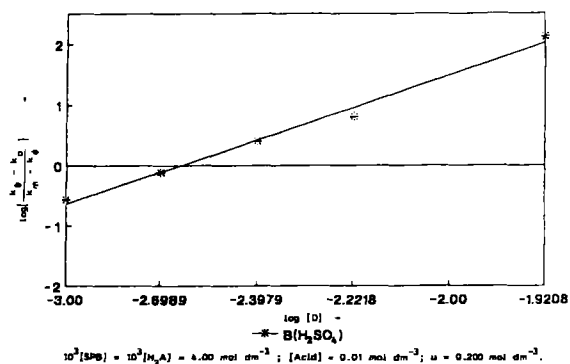
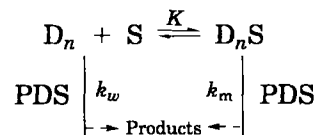


Figure 5 Plots of $\log \left\{ \frac{k_{\phi} - k_w}{k_m - k_{\phi}} \right\}$ versus $\log [D]$.



rate law for this scheme comes out as,

$$k_{\phi} = \frac{k_w + k_m K [D_n]}{1 + K [D_n]}$$

substituting for $[D_n] = (C_D - \text{CMC})/N$, the above equation takes the form,

$$k_{\phi} = \frac{k_w + k_m (K/N) (C_D - \text{CMC})}{1 + (K/N) (C_D - \text{CMC})}$$

where C_D is the concentration of the detergent and N is aggregation number of micelle. In these reactions k_m is taken as zero since inhibition took place even at very high concentration of surfactant, rearranging the above equation,

$$[(k_w/k_{\phi}) - 1] = (K/N)[C_D - \text{CMC}] \quad (22)$$

Plot of $[(k_w/k_{\phi}) - 1]$ vs. $(C_D - \text{CMC})$ should give a straight line which has been realized in the present study thus accounting for SDS inhibition. Binding constants (K) for SDS—PDS interactions have been evaluated and corresponding thermodynamic parameters are presented in Table IX. The ΔS values of K coupled with linearity of $\log k_{\phi}$ vs. $(D)^{-1}$ point out the importance of electrostatic interactions as well as hydrophilic interactions in the mechanism of oxidation.

Table VIII Effect of Triton-X on PDS—H₂A System in Various Acid Media. [PDS] = 0.02 mol dm⁻³; [H₂A] = 0.002 mol dm⁻³; and 10³[H₂SO₄] = 10³[HClO₄] = 2.4 mol dm⁻³

[Triton-X] %(v/v)	10 ⁴ k _φ (min ⁻¹)			
	H ₂ SO ₄ Medium		HClO ₄ Medium	
	298 K	308 K	298 K	308 K
0.15	2.41	6.17	3.02	6.48
0.25	2.48	6.26	3.13	6.64
0.35	2.56	6.34	3.27	6.83
0.45	2.68	6.40	3.46	7.06
0.55	2.87	6.41	3.75	7.37
0.60	2.92	6.45	3.94	7.51
0.65	2.96	6.46	4.08	7.63
0.75	3.00	6.47	4.23	7.78
0.85	3.02	6.48	4.33	7.87
0.95	3.03	6.49	4.37	7.93
1.05	3.04	6.49	4.39	7.95

Table IX Binding Constants (K) and Thermodynamic Parameters in PDS—H₂A System

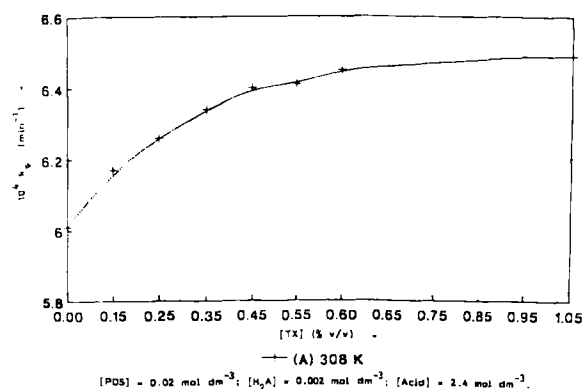
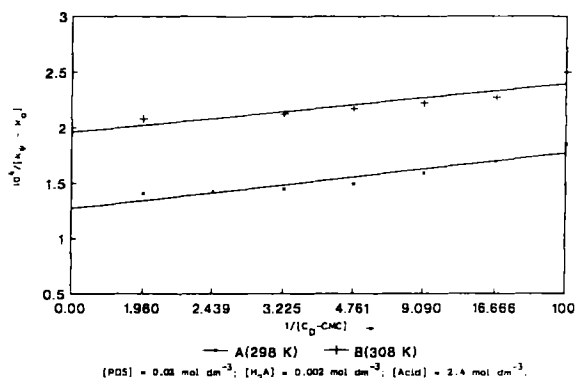
Medium	K at 298 K	ΔH KJ mol ⁻¹	ΔG KJ mol ⁻¹	$-\Delta S$ JK ⁻¹ mol ⁻¹
(A) SDS system				
H ₂ SO ₄	14.08	34.09	6.53	136.30
HClO ₄	19.40	26.51	7.32	113.54
(B) Triton-x system				
10 ⁻³ K at 298 K				
H ₂ SO ₄	3.72	30.96	20.31	35.74
HClO ₄	1.56	28.30	18.16	34.03

Mechanism of Oxidation of H₂A in the Presence of Triton-X

The data presented in Table VIII reveal that the rate of oxidation is catalyzed by Triton-X (Fig. 6). It could also be further noted that the plots of $(k_{\phi} - k_w)^{-1}$ vs. $(C_D - CMC)^{-1}$ were linear indicating the applicability of cooperative model to explain the catalytic path of Triton-x in the oxidation of H₂A by PDS (Fig. 7). Binding constants (K), rate constant (k_m), and corresponding activation parameters have been presented in Tables IX and X. The entropies of activation values (ΔS^\ddagger) probably point out the importance of hydrophilic interactions during micelle substrate (H₂A) binding. The relatively lesser ΔS^\ddagger value of HClO₄ system over H₂SO₄ may be explained due to a lesser hindrance of anion present in acid during the hydrophilic interactions. It is also pertinent to note that the rate of oxidation in the presence of triton-x is faster in the solvent of low dielectric constant and the observation is much more effective as compared to uncatalyzed path. These observations are in accordance with Laidler-Eyring theory and hence the more plausibility of anion-dipole type mechanism to be operative in PDS-H₂A system.

Reactions in the Presence of Cationic Micelles (CTAB)

Data presented in Table III for SPB—H₂A system reveal that rate of oxidation is not significantly af-

**Figure 6** Plots of k_{ψ} versus T_x (%V/V).**Figure 7** Plots of $\frac{1}{[k_{\psi} - k_0]}$ versus $\frac{1}{[C_D - CMC]}$.

ected by cationic micelle [CTAB]. This aspect probably points out the absence of anionic species in SPB—H₂A reaction.

All the efforts to study PDS—H₂A system in CTAB media have been unsuccessful since the reaction mixture developed turbidity during the kinetic study.

CONCLUSION

The reaction rates are sensitive to solvent and applicability of Amis theory in SPB—H₂A system and Laidler-Eyring theory in PDS—H₂A system, which lead to the formulation of cation-dipole and anion-dipole in the rate limiting steps, respectively.

A perusal of literature revealed that anionic species are stabilized by cationic micelles, cationic species by anionic micelles, and neutral molecules by non-ionic micelles and accordingly exhibit catalytic effect [28,29]. On the basis of this discussion catalytic activity of SDS, could be explained probably due to the stabilization of (SPBL)⁺ in transition state of SPB—H₂A reaction. Similarly inhibitory effect of SDS and catalytic effect of Triton-x in PDS—H₂A system could be explained due to electrostatic repulsion arising from anionic PDS species and SDS (or negative charge developed on polyoxyethylene group of Tx).

Table X Specific Rate Constants and Activation Parameters of PDS—H₂A System in Micellar Media

Medium	$10^4 k(\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1})$ at 298 K	ΔH^\ddagger KJ mol ⁻¹	ΔG^\ddagger KJ mol ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹
(A) Triton-x system				
H ₂ SO ₄	3.00	56.19	93.10	123.89
HClO ₄	4.26	43.69	92.24	162.92
(B) In SDS system specific rate constant is assumed to be minimum(almost zero)				

Inhibition of PDS oxidation of H₂A by both the micelles (SDS and Tx) at CMC and in the acid media (beyond 9.6×10^{-4} M HClO₄ and H₂SO₄) could be probably explained due to the repulsive interactions arising from negatively charged surface of SDS (a partial negative charge developed on polyoxy ethylene moiety of Tx) and ascorbic anion (HA⁻), a coanion present in trace amounts under reaction conditions.

Apart from electrostatic interactions, hydrophobic interaction also appeared to be important which could be seen from entropy of activation values also.

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