

Research Article

Kinetics and Mechanism of Electron Transfer Reactions: Oxidation of Sulfanilic Acid by Peroxomonosulfate in Aqueous Acidic Medium

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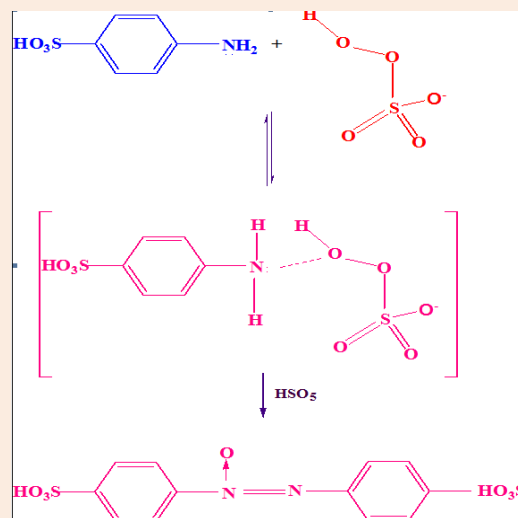
Abstract

The kinetics and mechanism of oxidation of sulfanilic acid by peroxomonosulfate have been studied in acid medium. Accounting for all such observations, a plausible reaction mechanism has been suggested. The activation parameters such as energy and entropy of activation have been calculated to be $(17.09 \pm 0.04) \text{ kJ mol}^{-1}$ and $(-220.8 \pm 0.21) \text{ JK}^{-1} \text{ mol}^{-1}$ respectively employing Eyring equation. The oxidation product of sulfanilic acid has been spectrally confirmed to be azoxybenzene-4-4'-disulfonic acid.

Keywords: Kinetics, Mechanism, Oxidation, Sulfanilic Acid, Peroxomonosulfate.

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**Introduction**

Peroxoacids are considered potential oxidizing agents of considerable significance. Peroxomonosulfate is a hydrolytic product of peroxodisulfate and is considered to be much better oxidant than its parent analogue. Peroxomonosulfate, in fact, is a substituted compound of hydrogen peroxide of which one of the hydrogens is replaced by $-\text{SO}_3$ group. This acid is dibasic and its ionizable protons resemble to that of H_2SO_4 and H_2O_2 respectively. These peroxides are the oxygen donors in reactions of organic and inorganic substrates in bleaching contaminants. The peroxide bond in this per-acid is mainly responsible of its reactions. H_2O_2 which is also considered to be a strong bleaching oxidizing agent is a parent analogue of such an important class of peracids. However, the chemistry of peroxomonosulfate is less understood than that of peroxodisulfate. Since we are engaged with studies of kinetics of peroxomonosulfate oxidations [1-6], it is thought proper to study the oxidation reaction of sulfanilic acid by employing this oxidant to understand the pattern of reactivity of the latter in view of its importance in drugs and dyes industries.

A large number of kinetic studies of oxidations employing peroxomonosulfate as an oxidant have been reported [7-16]. Interestingly, most of the peroxodisulfate reactions are chain reactions as the sulfate ion free radical is produced both in thermal and photochemical reactions whereas no such free radical is reported so far in the redox reactions of peroxomonosulfate.

It is this unique nature of this peracid that prompted us to understand its redox behavior towards sulfanilic acid with the view whether or not the reaction is a free radical reaction. An earlier report [17] in higher pH region for the oxidation of sulfanilic acid by peroxomonosulfate mentions about its reaction. However, we attempted to study this reaction to understand more about the pattern of its reactivity towards sulfanilic acid in aqueous acid medium to understand whether or not this reaction has any different reactivity pattern.

Experimental

Materials and methods

Peroxomonosulfate was a triple salt of ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) which is commercially known by the trade name Oxone. The sample obtained from Aldrich was employed as supplied. The solution of peroxomonosulfate was prepared by dissolving the requisite amount in doubly distilled water and was further standardized iodometrically [18-19]. The sample was found ~96% pure. Since the aqueous solution of peroxomonosulfate is quite stable at ambient temperature, afresh solutions of peracid were always employed both for analytical as well as kinetic studies.

Sulfanilic acid (EMerck) solution was prepared by dissolving the requisite amount of the acid in doubly distilled water and the solution was kept in bottles painted black from the outside at refrigerated temperature ($\sim 5^\circ\text{C}$). Further, it has also been observed that solution of sulfanilic acid is stabilized by addition of very dilute alkali solution.

Other reagents were of AnalaR or G.R. grade and were employed as received. Doubly distilled water was employed throughout the study; second distillation was in the presence of alkaline KMnO_4 in an all glass still. However, trace metal-ion catalysis is reported in case of peroxomonosulfate reactions. Therefore, a few reactions were also carried out in the presence of triple distilled water (triple distilled water was obtained by redistilling doubly distilled water in the presence of edta), no such trace metal ion catalysis was observed. Therefore, all kinetics studies were made in doubly distilled water.

Stoichiometry and product analysis

The stoichiometry of the reaction was studied by employing excess concentration of peroxomonosulfate (heretofore written as PMS) over that of sulfanilic acid (henceforth written as SA) in acid medium. The reaction was allowed to occur in a thermostated water bath for ca.10h and unreacted peroxomonosulfate was estimated iodometrically. It was found that two moles of peroxomonosulfate reacts with a mole of sulfanilic acid corresponding to a stoichiometry of the reaction of two moles of peroxomonosulfate with a mole of sulfanilic acid.

The confirmation of stoichiometry was further made by undertaking kinetics of the reaction under observed stoichiometric conditions. Second order plots of $1/[\text{PMS}]_t$ vs time were made (Fig-1) and the rate constants calculated from such plots were found in agreement with the second order rate constants obtained by other methods as mentioned in Table-1.

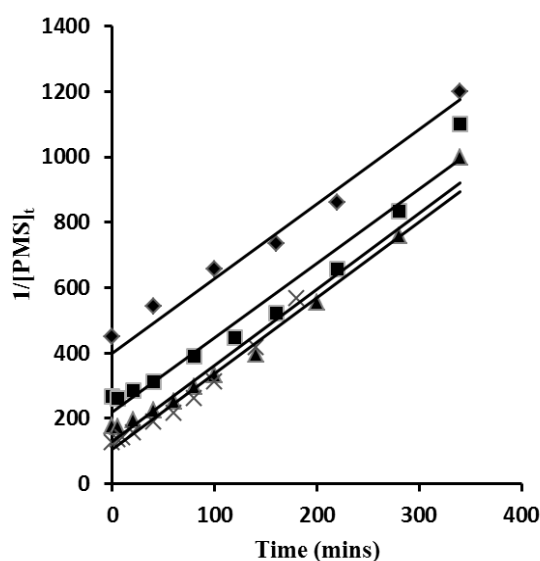


Figure 1 Stoichiometric plots in sulfanilic acid and peroxomonosulfate reaction

$$\blacklozenge[\text{PMS}] = [\text{SA}] = 2.0 \times 10^{-3}; \blacksquare[\text{PMS}] = [\text{SA}] = 4.0 \times 10^{-3};$$

$$\blacktriangle[\text{PMS}] = [\text{SA}] = 6.0 \times 10^{-3}; \times[\text{PMS}] = [\text{SA}] = 8.0 \times 10^{-3} \text{ mol dm}^{-3};$$

$$[\text{H}_2\text{SO}_4] = 0.05 \text{ mol dm}^{-3} \text{ and } 35^\circ\text{C}$$

Table-1, Initial rates, pseudo first order rate constants and second order rate constants in the reaction of Sulfanilic Acid with peroxomonosulfate in acid medium. $[\text{H}_2\text{SO}_4] = 0.05 \text{ mol dm}^{-3}$, 35°C

$10^2[\text{SA}]$ mol dm^{-3}	$10^3[\text{PMS}]$ mol dm^{-3}	$10^6 (k_i)$ $\text{mol dm}^{-3}\text{s}^{-1}$	$10^4 (k')$ s^{-1}	$10^2 (k)$ $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$
1.0	1.0	0.19	–	1.91 (1.92)
1.0	2.0	0.38	–	1.91(1.91)
1.0	3.0	0.57	–	1.91(1.89)
1.0	4.0	0.77	–	1.91(1.92)
1.0	5.0	0.95	–	1.91(1.9)
1.0	6.0	1.13	–	1.91(1.9)
1.0	7.0	1.33	–	1.91(1.9)
1.0	8.0	1.54	–	1.91(1.92)
1.0	9.0	1.71	–	1.91(1.9)
1.0	10	1.92	–	1.91(1.92)
2.0	0.2	–	3.84	(1.92)
2.0	0.4	–	3.84	(1.92)
2.0	0.6	–	3.84	(1.92)
2.0	0.8	–	3.84	(1.92)
2.0	1.0	–	3.84	(1.92)
2.0	2.0	–	3.84	(1.92)
0.2	2.0	0.077	–	(1.91)
0.3	2.0	0.11	–	1.91(1.9)
0.4	2.0	0.15	–	1.91(1.91)
0.6	2.0	0.23	–	1.91(1.91)
0.8	2.0	0.30	–	1.91(1.88)
1.0	2.0	0.38	–	1.91(1.91)
1.5	2.0	0.57	–	1.91(1.89)
2.0	2.0	0.75	3.83	1.91(1.91)
2.5	2.0	0.96	4.79	1.91(1.92)
3.0	2.0	1.13	5.75	1.91(1.91)

Figures in parenthesis are calculated second order rate constants.

Further the oxidation product of sulfanilic acid to be azoxybenzene-4-4'-disulfonic acid was identified and established spectrally.

The reaction product was eluted by thin layer chromatography. Thin layer chromatograms were conducted on Merck silica gel G plates in methyl alcohol: acetonitrile (7:3) and in the column chromatographic fractionations silica gel (60-120 mesh) was used. Spots on TLC plates were visualized by spraying with 2% ceric ammonium sulfate in 2N H_2SO_4 or with iodine vapors.

The IR spectrum of the product showed absorption bands at 1130 cm^{-1} and 1040 cm^{-1} indicating two stretching bands of $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$. Also, absorption at 1320 cm^{-1} and 1420 cm^{-1} respectively indicate the presence of $-\text{N}=\text{N}\rightarrow\text{O}$ strong

stretching bands. The bands at 1500 cm^{-1} and 1230 cm^{-1} indicates respectively -N=N- and -C-N= stretching bands of azoxy group.

^1H NMR spectrum was also obtained in DMSO- d_6 employing 300MHz spectrometer employing TMS as reference. A singlet at $\delta 2.535\text{ ppm}$ shows the presence of $\text{-SO}_3\text{H}$ group. Peaks in the range $\delta 7\text{-}8\text{ ppm}$ are owing to aromatic rings.

The mass spectrum of this product displayed a peak at m/z 356 after the loss of two hydrogens from its molecular ion of 358.

Kinetic procedure

The reaction mixtures containing all other reaction ingredients except peroxomonosulfate were taken in glass stoppered Erlenmeyer flasks painted black from the outside to check any photochemical decomposition. These flasks were suspended in a water-bath thermostated at $35 \pm 0.1^\circ\text{C}$ unless stated otherwise. The temperature pre-equilibrated solution of peroxomonosulfate was added in to reaction mixture to initiate the reaction. The time of initiation of the reaction was recorded when half of the peroxomonosulfate contents from the pipette were released into the reaction mixture. An aliquot of the reaction mixture (5 cm^3) was withdrawn at different time intervals and then discharged into freshly prepared ice cold potassium iodide ($\sim 10\%$) solution. The liberated iodine was titrated against thiosulfate solution employing starch as an indicator.

Initial rates (k_i , $\text{mol dm}^{-3}\text{ s}^{-1}$) were computed by employing glass mirror method [20]. Also, first order plots (k' , s^{-1}) were made for reactions where the concentration of sulfanilic acid was at least more than 10 times the concentration of peroxomonosulfate. Second order plots were also made for comparable concentrations of the reactants. The rates in triplicate were reproducible to within $\pm 5\%$.

Results and Discussion

Peroxomonosulfate concentration dependence

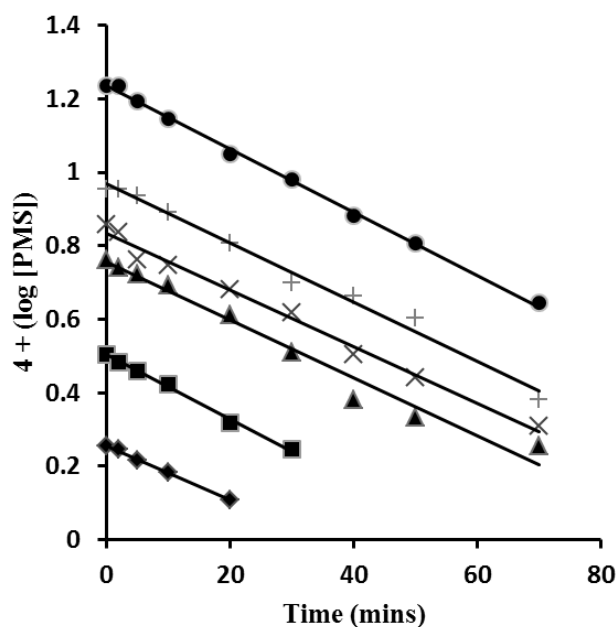


Figure 2 Pseudo first order plots in sulfanilic acid and peroxomonosulfate reaction

$[SA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.05 \text{ mol dm}^{-3}$ and 35°C

$[PMS] =$ (1) $\blacklozenge 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; (2) $\blacksquare 4.0 \times 10^{-4} \text{ mol dm}^{-3}$;
 (3) $\blacktriangle 6.0 \times 10^{-4} \text{ mol dm}^{-3}$; (4) $\times 8.0 \times 10^{-4} \text{ mol dm}^{-3}$
 (5) $+ 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ (6) $\bullet 2.0 \times 10^{-3} \text{ mol dm}^{-3}$

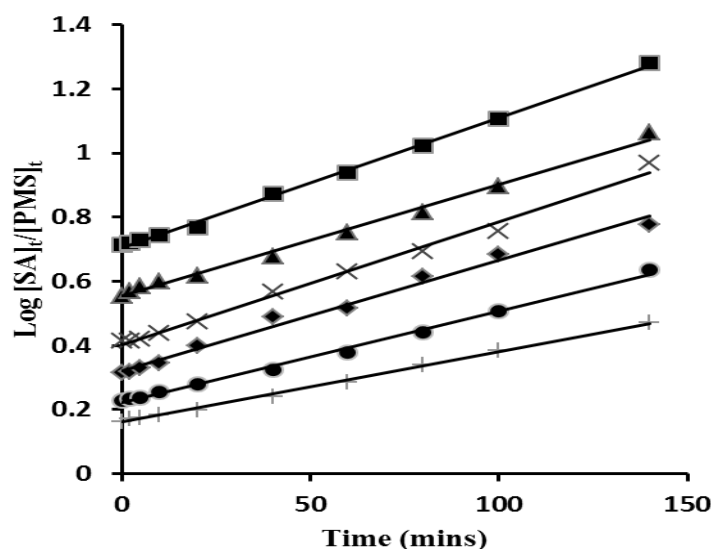


Figure 3 Second order plots in sulfanilic acid and peroxomonosulfate reaction

$[SA] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.05 \text{ mol dm}^{-3}$; and 35°C

$[PMS] =$ (1) $+ 3.0 \times 10^{-3}$; (2) $\bullet 4.0 \times 10^{-3}$; (3) $\blacklozenge 5.0 \times 10^{-3}$;
 (4) $\times 6.0 \times 10^{-3}$; (5) $\blacktriangle 7.0 \times 10^{-3}$; (6) $\blacksquare 8.0 \times 10^{-3} \text{ mol dm}^{-3}$

Sulfanilic acid concentration dependence

The concentration of sulfanilic acid was varied from $(2.0 \times 10^{-3} \text{ to } 3.0 \times 10^{-2}) \text{ mol dm}^{-3}$ keeping constant concentrations of other reaction ingredients *viz.* $[PMS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 35°C .

Initial rates were plotted against the concentration of sulfanilic acid; a straight line passing through the origin confirms first order dependence with respect to the substrate. Similarly second order plots of $\log [PMS]_t/[SA]_t$ or $\log [SA]_t/[PMS]_t$ versus time were also made for comparable concentrations of the reactants. Second order rate constants as collected in table-1 are in agreement.

It is, therefore, clear that the overall reaction is second order confirming to an empirical rate law (1)

$$-\frac{d[PMS]}{dt} = A [PMS]_T [SA]_T \quad (1)$$

where $[PMS]_T$ and $[SA]_T$ are the gross analytical concentrations of peroxomonosulfate and sulfanilic acid respectively, and 'A' is an empirical rate constant.

Hydrogen ion concentration dependence

The dependence of hydrogen ion concentration on the rate of reaction was studied by employing perchloric acid keeping constant concentrations of other reaction ingredients *viz.* $[PMS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[SA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.05 \text{ mol dm}^{-3}$ and $[I] = 1.0 \text{ mol dm}^{-3}$ at 35°, 40° and 45°C respectively. The rate decreases with increasing concentration of hydrogen ion. Ionic strength (I) was adjusted constant by employing lithium perchlorate.

Effect of ionic strength (I)

Effect of ionic strength was studied by employing lithium perchlorate or sodium nitrate at constant concentrations of reaction ingredients *viz.* $[SA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[PMS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 35°C. The rate increases with increasing concentrations with either $LiClO_4$ or $NaNO_3$ (**Figure 4**).

Effect of temperature

The effect of temperature was studied at 35°, 40° and 45°C respectively keeping fixed concentrations of reaction ingredients *viz.* $[SA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[PMS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[H^+] = 0.05 \text{ mol dm}^{-3}$ at $I=1.0 \text{ mol dm}^{-3}$. The energy and entropy of activation respectively were evaluated by employing Eyring eqn [21] to be $(17.09 \pm 0.04) \text{ kJ mol}^{-1}$ and $(-220.8 \pm 0.21) \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

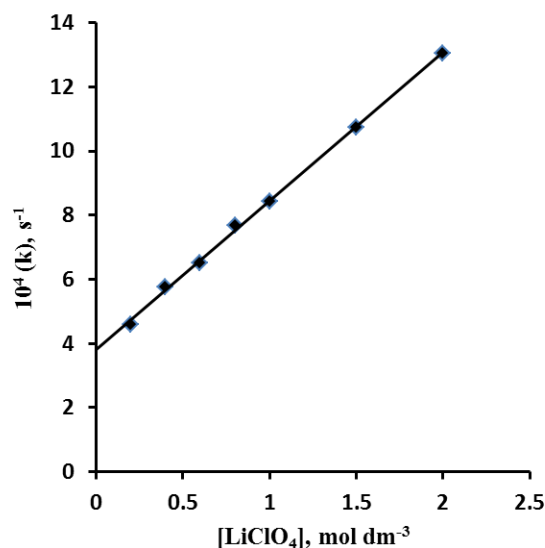


Figure 4 Variation of $LiClO_4$ in sulfanilic acid and peroxomonosulfate reaction
 $[PMS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.05 \text{ mol dm}^{-3}$;
 $[SA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and 35°C

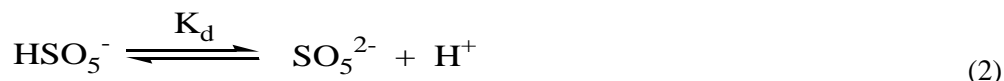
Test of free radicals

The test of formation of free radicals was made by adding acrylic acid in the reaction mixture. The polymerization of acrylic acid monomer was not observed as no white sediment was formed even after 2h. It appears that as soon as free

radical if formed, it reacts in the solvent cage before finding time to diffuse out of it to attack monomer for polymerization.

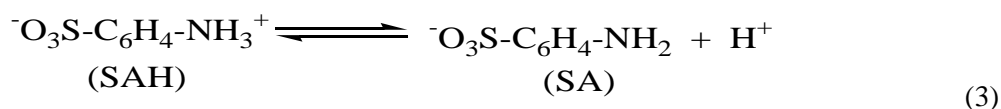
Discussion

The kinetic order with respect to peroxomonosulfate and sulfanilic acid is one each conforming to over all reaction to be second order. If pK_1 and pK_2 of the per-acid are any guide, the latter mainly exists as HSO_5^- and SO_5^{2-} species in the solution depending upon the pH.

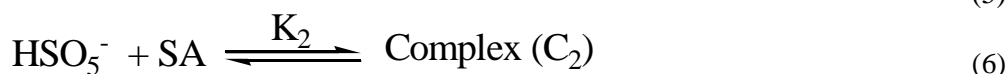
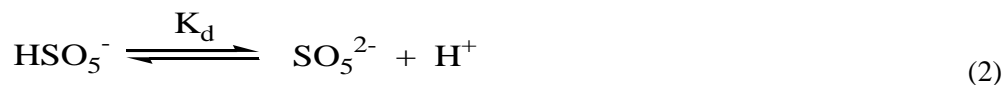


HSO_5^- is predominantly reactive species of the per-acid and mainly exists in acidic medium up to pH 6. If pK_1 (K_d) is taken into account, the concentration of HSO_5^- species is more than 99% than SO_5^{2-} and at $\text{pH} < 6$. Since the kinetics of oxidation of sulfanilic acid by peroxomonosulfate has been studied in acid medium ($[\text{H}^+] > 0.05 \text{ mol dm}^{-3}$). HSO_5^- species is predominant and it is certainly more reactive than SO_5^{2-} species.

Sulfanilic acid also predominantly exists in its molecular state ($K_a = 6.03 \times 10^{-4}$ at 25°) if pK_a is any guide.



Thus if first order with respect to per-acid and sulfanilic acid each and retarding effect of hydrogen ion concentration are taken into account, the following reaction mechanism consisting of step (2) and steps (4) to (7) together can be envisaged in conformity of experimental observations.



The loss of peroxomonosulfate (HSO_5^-) leads to the rate law (8)

$$-\frac{d[\text{PMS}]}{dt} = \left(k_1'K_1' + \frac{k_2'K_2'K_d}{[\text{H}^+]} \right) \frac{[\text{PMS}]_T[\text{SA}][\text{H}^+]}{[\text{H}^+] + K_d + [\text{SA}](K_1' + K_2'K_d)} \quad (8)$$

Where $[\text{PMS}]_T$ and $[\text{SA}]$ are gross analytical and equilibrium concentrations of peroxomonosulfate and sulfanilic acid respectively.

The inequalities such as $[\text{H}^+] \gg K_d$ and $[\text{SA}](K_1' + K_2'K_d) \ll ([\text{H}^+] + K_d)$ are valid in acid medium in the light of following two observations.

A plot of $1/\text{rate}$ versus $1/\text{SA}$ yielded a straight line passing through the origin ruling out any complex formation between oxidant and substrate. Secondly kinetic order with respect to organic acid has been found to be one. Thus the rate law (8) in view of these facts can be reduced to eqn (9)

$$-\frac{d[\text{HSO}_5^-]}{dt} = \left(k_1'K_1 + \frac{k_2'K_2K_d}{[\text{H}^+]} \right) [\text{PMS}]_T [\text{SA}]_T \quad (9)$$

Such a rate law (9) is in conformity of the observed kinetic results.

Further, K_1 and K_2 are insignificant equilibrium constants in view of the facts that intermediates complexes 'C₁' and 'C₂' are established neither kinetically nor spectrally. Thus the rate law (9) is further reduced to eqn (10) or (11)

$$-\frac{d[\text{HSO}_5^-]}{dt} = \left(k_1 + \frac{k_2K_d}{[\text{H}^+]} \right) [\text{PMS}]_T [\text{SA}] \quad (10)$$

Where $k_1 = k_1'K_1$ and $k_2 = k_2'K_2$

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

A plot of ' k ' versus $[\text{H}^+]^{-1}$ was made from eqn (11) that yielded a straight line with non-zero intercept (Fig-5) (10^3) k_1 was calculated from the intercept to be 0.8, 1.4 and 1.9 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ respectively and similarly (10^3) k_2K_d was calculated from the slope to be 4.18, 4.67 and 5.26 s^{-1} at 35°, 40° and 45°C respectively and $I = 1 \text{ mol dm}^{-3}$. If K_d is taken into account, k_1 is significantly more than k_2 and rate is controlled by (HSO_5^- -SA) path and not by (SO_5^{2-} -SA) path of the reaction mechanism under experimental conditions.

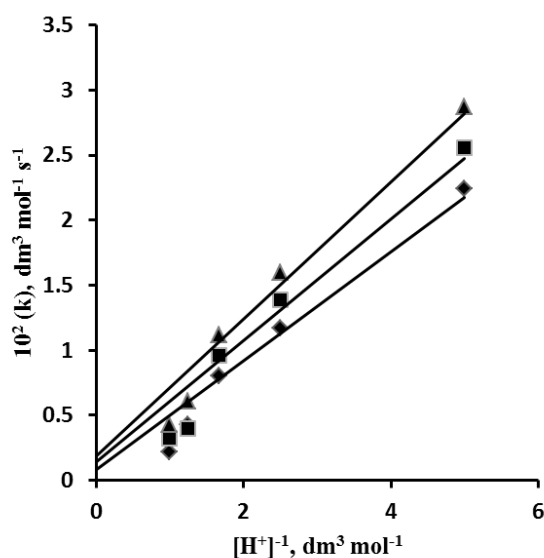


Figure 5 Plots of k versus $[\text{H}^+]^{-1}$ in sulfanilic acid and peroxomonosulfate reaction

$[\text{PMS}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 0.05 \text{ mol dm}^{-3}$;

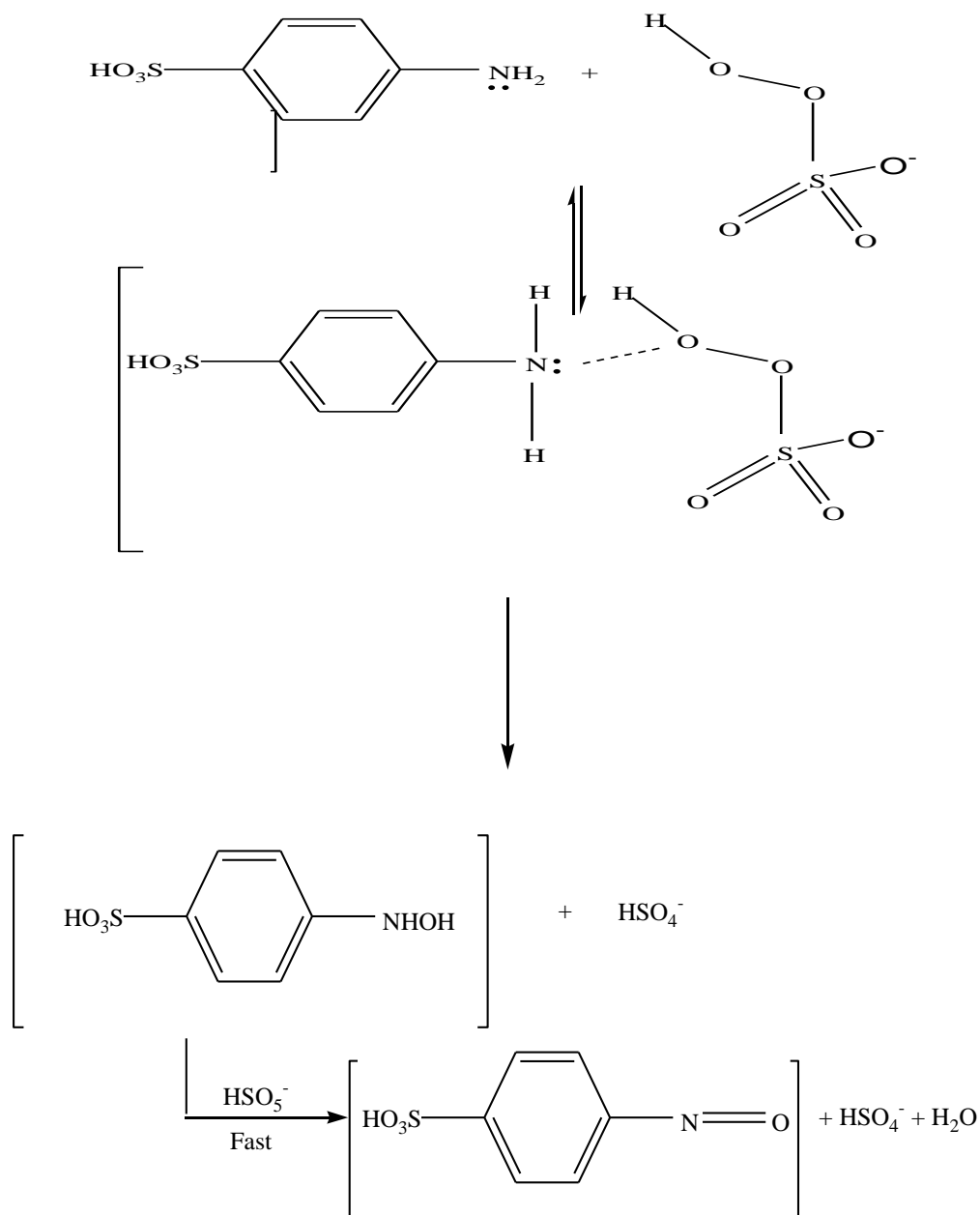
$[\text{I}] = 1.0 \text{ mol dm}^{-3}$; $[\text{SA}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$;

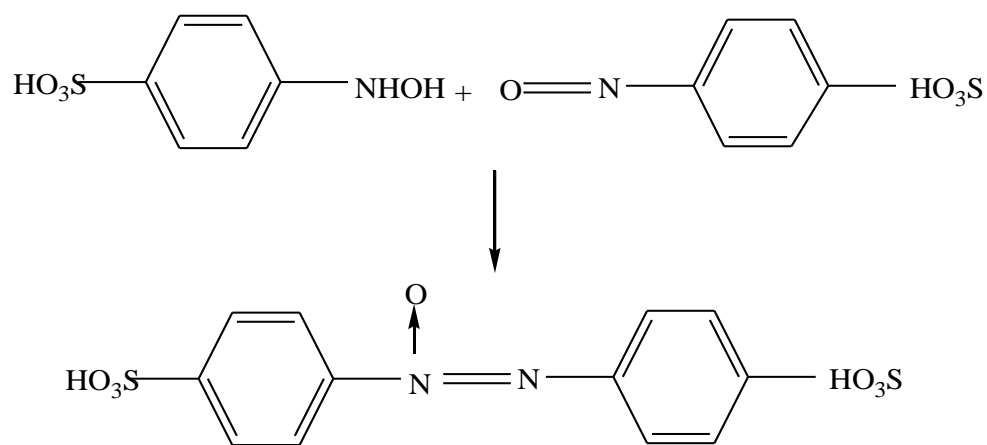
◆ 35°, ■ 40° and ▲ 45°C

The energy and entropy of activation for the reaction were calculated to be $(17.09 \pm 0.04) \text{ kJ mol}^{-1}$ and $(-220.8 \pm 0.21) \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. ΔS^\ddagger is significantly lower and negative which can be accounted for highly solvated transition state. Moreover, loss of degrees of freedom brings the transition state to a more ordered state.

The availability of free electron pair on the nitrogen atom makes sulfanilic acid to be a good nucleophilic reagent [22]. This nucleophilicity of the reagent to some extent is reduced owing to the presence of electron withdrawing $-\text{SO}_3\text{H}$ group. Sulfanilic acid as a nucleophile is protonated through amino group and as such the rate is significantly decreased.

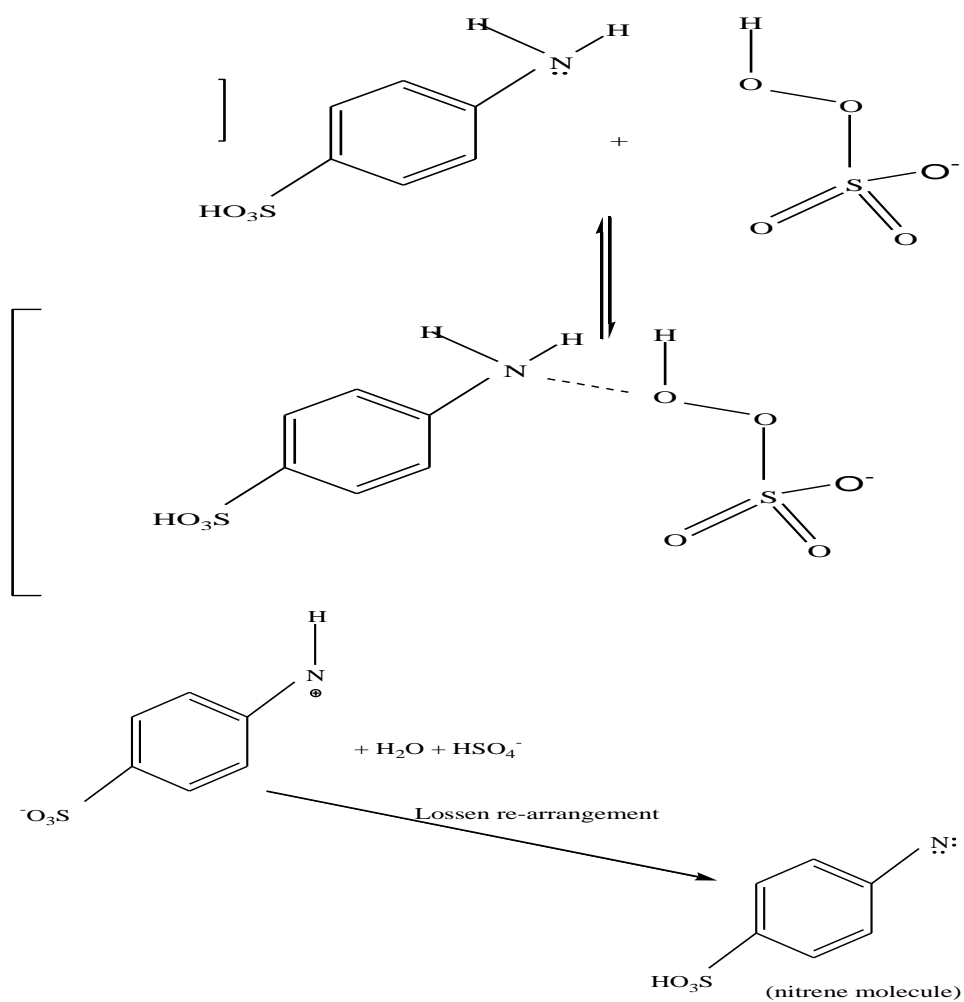
Thus the following scheme-I can account for the mode of electron transfer from sulfanilic acid to the oxidant to yield azoxybenzene-4,4'-disulphonic acid as the oxidation product.

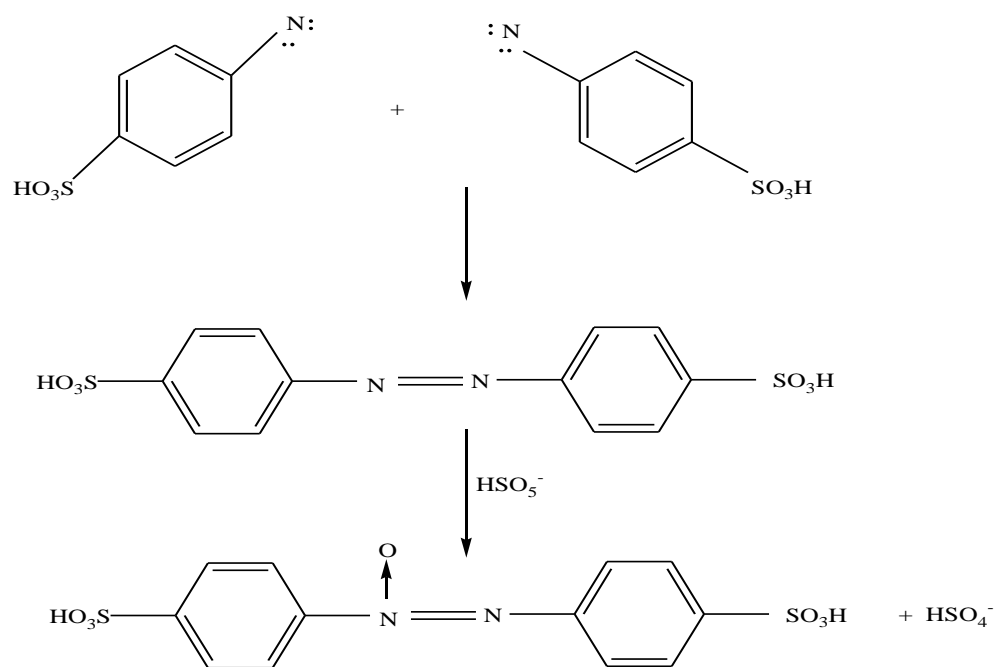




Thus the oxidation product of sulfanilic acid is azoxybenzene-4,4'-disulphonic acid.

An alternative proposal can also be suggested as in scheme-II as follows in which lossen re-arrangement [23] yields nitrene.





Although the formation of the oxidation product in these two schemes is adequately justified but distinction between these schemes is difficult unless intermediates are kinetically or spectrally distinguished. However, stoichiometric results in excess of per-acid correspond to such a product which has earlier been suggested [24] also. Azoxybenzene-4,4'-disulphonic acid has also been suggested to be the product [25] of oxidation of sulfanilic acid.

The azoxy product reported in oxidation of sulfanilic acid by hexacyanoferrate (III) with characterization of λ_{\max} at 433, 322 and 601.6 nm respectively, and such a dye was not observed in this reaction. Also $>C=O$ group despite extending conjugation does not show any λ_{\max} in the reaction eliminating formation of ketoazoxy dye in the title reaction [26].

Conclusion

The kinetic order with respect to peroxomonosulfate and sulfanilic acid is one each conforming to over all reaction to be second order and the oxidation product of sulfanilic acid is azoxybenzene-4,4'-disulphonic acid. If K_d is taken into account, k_1 is significantly more than k_2 and rate is controlled by (HSO_5^-SA) path and not by $(SO_5^{2-}-SA)$ path of the reaction mechanism under experimental conditions.

Acknowledgement

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