

Kinetics and Mechanism of Electron Transfer Reaction: Oxidation of Sulfanilic Acid by *N*-Chloro-*p*-Toluene Sulfonamide in Acid Perchlorate Medium

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The kinetics and mechanism of oxidation of sulfanilic acid by *N*-chloro-*p*-toluene sulfonamide (chloramine-T) have been studied in acid medium. The species of chloramine-T were analysed on the basis of experimental observations and predominantly reactive species was taken into account for proposition of most plausible reaction mechanism. The derived rate law (1) conforms to such a mechanism.

$$-\frac{d[\text{CAT}]}{dt} = \frac{kK_1[\text{RNHCl}][\text{SA}]}{K_1 + [\text{H}^+]} \quad (1)$$

All kinetic parameters were evaluated. Activation parameters such as energy and entropy of activation were calculated to be $(61.67 \pm 0.47) \text{ kJ mol}^{-1}$ and $(-62.71 \pm 2.48) \text{ JK}^{-1}\text{mol}^{-1}$ respectively employing Eyring equation.

Key Words : Kinetics, Mechanism, Oxidation, Sulfanilic acid, Chloramine-T

Introduction

The chemistry of *N*-halo-*p*-toluene sulphonamide¹⁻⁹ has been of much interest both in analytical as well as pharmaceutical chemistry. A number of papers on the pattern of its reactivity both in acid¹⁰⁻²⁷ and alkaline²⁸⁻³⁵ media have been the subject matter of its redox kinetics. The only problem in such reactions is about the proper speciation of its various species. However, reactions of chloramine-T are found to be very slow in alkaline medium and as a result most of such studies have employed transition metal ions as catalysts.

Sulfanilic acid considered to be an important reagent in synthesis of dyes³⁶ and sulfa drugs.^{37,38} The interaction between sulfanilic acid and chloramine-T appears to be an interesting study more particularly from the view point of speciation of chloramine-T species in acid medium. Such an interesting chemistry of chloramine-T, particularly as an oxidant, chlorinating reagents and analytical reagents have prompted us to undertake the title reaction from the following view points:

Chloramine-T is considered to be a potential oxidant in acid medium and has been frequently employed as an oxidimetric reagent in analytical chemistry. Our interest lies in the title study to find out such analytical conditions in such a manner that sulfanilic acid can be estimated quantitatively in solutions by chloramine-T either titrimetrically or spectrophotometrically.

Secondly, the title reaction appears to be an important probe mechanistically as this reagent is considered to be an important antiseptic and disinfectant reagent.

Thirdly, logical information regarding the speciation of chloramine-T species in acid medium can be ascertained.

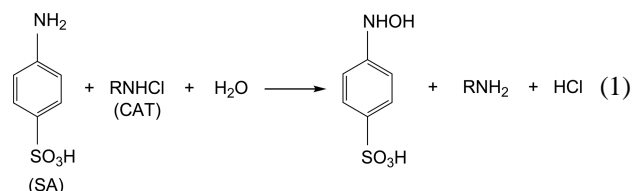
Experimental

Materials and Methods. Sodium salt of *N*-chloro-*p*-

toluene sulfonamide (E Merck) was used as received without any further treatment. The solution was prepared in doubly distilled water and was standardized iodometrically.^{39,40} Since the solution of chloramine-T is not stable, therefore, the solution was kept in bottles coated black from the outside. The solution of chloramine-T, if kept, in dark at refrigerated temperature ($\sim 5^\circ\text{C}$), the stability is enhanced considerably. Other reagents were either of AnalR or G.R. quality and were used as supplied.

Doubly distilled water was employed throughout the kinetic study; second distillation was from alkaline permanganate solution in an all glass assembly.

Stoichiometry and Product Analysis. The stoichiometry of the reaction was determined where excess chloramine-T concentration was taken over that of sulfanilic acid and HClO_4 0.1 mol dm^{-3} . These reactions were allowed to occur in a thermostated water-bath 30°C for *ca.* 8 h. Ensuring completion of the reaction, excess chloramine-T was estimated iodometrically that corresponded to the reaction as represented by Eqn. (1)



where $\text{R} = p\text{-CH}_3\text{-C}_6\text{H}_4\text{SO}_2\text{-}$

Toluene-*p*-sulfonamide (RNH_2) is one of the reaction products which was identified by its usual test and does not affect the reaction rate (Figure 1).

Further the oxidation product to be *N*-hydroxylamino-4-sulphonic acid was identified and established to be *N*-hydroxylaminobenzene-4-sulphonic acid.

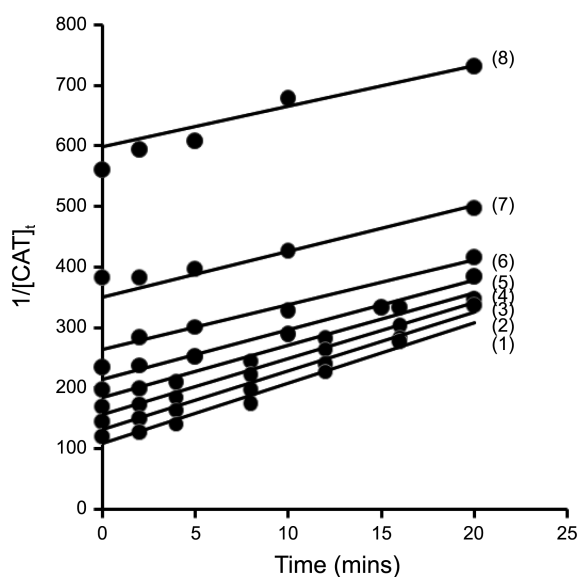


Figure 1. Stoichiometric plots in the reaction of CAT and sulfanilic acid. $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$ and 30°C . $[\text{SA}] = [\text{CAT}] = (1) 2.0 \times 10^{-3}$; (2) 3.0×10^{-3} ; (3) 4.0×10^{-3} ; (4) 5.0×10^{-3} ; (5) 6.0×10^{-3} ; (6) 7.0×10^{-3} ; (7) 8.0×10^{-3} ; (8) $10 \times 10^{-3} \text{ mol dm}^{-3}$.

The reaction product, *N*-hydroxylaminosulfonic acid was eluted by thin layer chromatography. Thin layer chromatograms were conducted on Merck silica gel G plates in methyl alcohol:ethyl acetate (8:2) and in the column chromatographic fractionations silica gel (60-120 mesh). Spots on TLC plates were visualized by spraying with 2% ceric ammonium sulfate in 2 N H_2SO_4 or with iodine vapours.

IR spectrum of the product showed absorption band at 3415 cm^{-1} and 3480 cm^{-1} indicating two stretching bands of amine. Absorption at 3552 cm^{-1} indicates the presence of -OH strong stretching band. The bands at 1618 cm^{-1} and 1643 cm^{-1} respectively indicate the C=C stretching frequency of aromatic group. The absorption band at 1094 cm^{-1} shows the presence of stretching frequency of =C-NH.

^1H NMR spectrum was also obtained in $\text{DMSO-}d_6$ employing 300 MHz spectrometer using TMS as reference as in. In ^1H NMR spectrum signal at $\delta 4.039$ (s) ppm is due to -NH group of amine. Two singlets are obtained at $\delta 2.5$ ppm and $\delta 2.06$ ppm showing the presence of -OH group.

The mass spectrum of this product displayed a peak at m/z 187 after the loss of two hydrogens from its molecular ion at 189. The elemental analysis was in agreement with a molecular formula $\text{C}_6\text{H}_7\text{O}_4\text{NS}$.

The product *N*-hydroxylaminosulfonic acid in acid medium does not undergo any further oxidation under the present kinetics conditions.

Kinetic Procedure. Kinetics of the reaction was studied by taking all the reaction ingredients except chloramine-T in glass stoppered black coated Erlenmeyer flasks which were suspended in a water-bath thermostated at $30 \pm 0.1^\circ\text{C}$ until and unless specified otherwise. Temperature pre-equilibrated solution of chloramine-T (heretofore written as CAT) was added into reaction mixture to initiate the reaction. However, order of addition of the reagents for initiation of

the reaction either by sulfanilic acid or chloramine-T has no effect on the kinetics of the reaction. The time of initiation of the reaction was recorded when 50% of the contents from the pipette were discharged into the reaction mixture.

An aliquot (5 cm^3) of the reaction mixture was withdrawn periodically to assay the remaining chloramine-T at different time intervals iodometrically. None of the reaction ingredients interfered with iodometric method.

Initial rates were computed by employing plane mirror method.⁴¹ Also, pseudo first order plots were made wherever reaction conditions permitted ($[\text{SA}] \gg 10 [\text{CAT}]$). Second order plots were also made in reactions of comparable concentrations of reactants. The rates in triplicate were reproducible to within $\pm 5\%$.

Results and Discussion

Chloramine-T Dependence. The concentration of chloramine-T was varied from 1.0×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ at two but fixed concentrations of sulfanilic acid (heretofore written as SA) to be 5.0×10^{-3} and $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ keeping constant concentrations of other reaction ingredients *viz.* $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ at 30°C . Initial rates (k_i , $\text{mol dm}^{-3} \text{ s}^{-1}$) were computed and a plot of initial rate *versus* concentration of chloramine-T was made that yielded a straight line passing through the origin indicating first order dependence with respect to chloramine-T. Further confirmation of the first order with respect to chloramine-T was made by undertaking, certain reactions under pseudo first order conditions and a plot of $\log [\text{CAT}]_t$ *versus* time was made (Figure 2). The pseudo first order rate constants (k' , s^{-1}) evaluated from these plots were found to be independent of gross initial concentrations of the oxidant. Moreover, second order plots were also constructed for comparable concent-

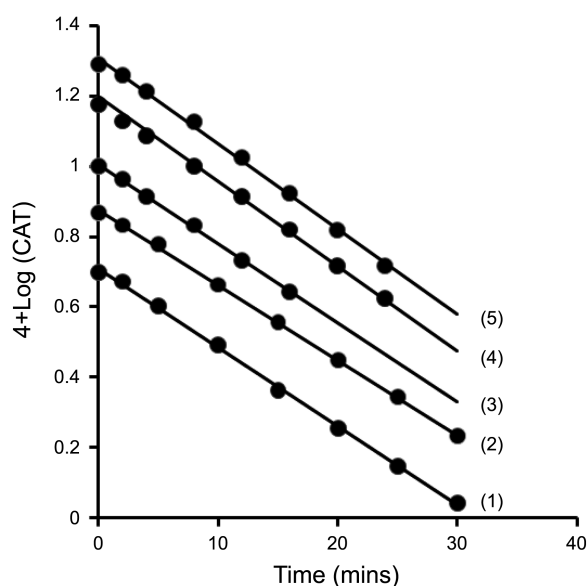


Figure 2. Pseudo first order plots in the reaction of CAT and sulfanilic acid. $[\text{SA}] = 0.02 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$ and 30°C . $[\text{CAT}] = (1) 5.0 \times 10^{-4}$; (2) 7.5×10^{-4} ; (3) 1.0×10^{-3} ; (4) 1.5×10^{-3} ; (5) $2.0 \times 10^{-3} \text{ mol dm}^{-3}$.

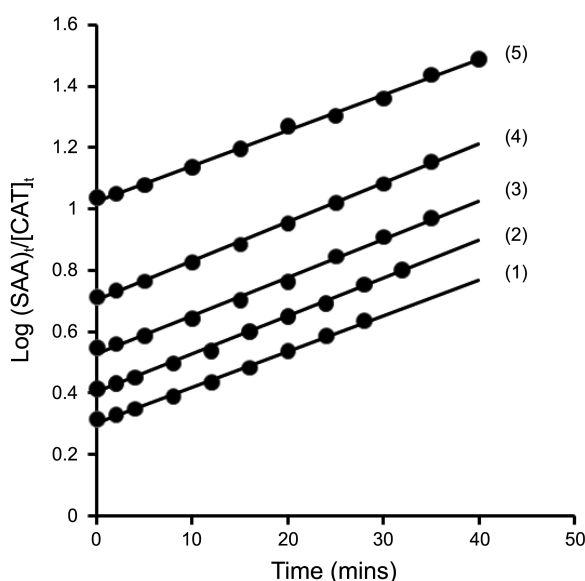


Figure 3. Second order plots in the reaction of CAT and sulfanilic acid. $[SA] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[HClO_4] = 0.1 \text{ mol dm}^{-3}$ and 30°C . $[CAT] = (1) 1.0 \times 10^{-3}$; (2) 2.0×10^{-3} ; (3) 3.0×10^{-3} ; (4) 4.0×10^{-3} ; (5) $5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

rations of chloramine-T and sulfanilic acid by plotting $\log [CAT]_t/[SA]_t$ versus time or $\log [SA]_t/[CAT]_t$ versus time (Figure 3).

The second order rate constants evaluated from these second order plots were in good agreement with those obtained from initial rates and first order rate constants respectively (Table 1).

Sulfanilic Acid Concentration Dependence. The concentration of sulfanilic acid was varied from 1.0×10^{-3} to $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ at two fixed concentrations of $[CAT]$ viz. 2.0×10^{-3} and $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ respectively. Also, variation in $[SA]$ from 1.0×10^{-2} to $4.5 \times 10^{-2} \text{ mol dm}^{-3}$ at two fixed concentrations of $[CAT]$ viz. 1.0×10^{-3} and $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ respectively was made keeping constant concentrations of other reaction ingredients viz. $[HClO_4] = 0.1 \text{ mol dm}^{-3}$ at 30°C .

Initial rates were calculated and these were plotted against the concentration of sulfanilic acid that yielded a straight line passing through the origin indicating first order with respect to sulfanilic acid too to be one. Similarly first order and second order plots were also made wherever reaction conditions permitted.

Considering first order dependence with respect to the oxidant and substrate respectively, an empirical rate Eq. (2) can be envisaged-

$$-\frac{d[CAT]}{dt} = A[CAT][SA] \quad (2)$$

where 'A' is an empirical constant. $[CAT]$ and $[SA]$ are gross analytical concentrations of chloramine-T and sulfanilic acid respectively.

Hydrogen Ion Dependence. The effect of hydrogen ion concentration was studied by employing perchloric acid. The concentration of hydrogen ion was varied from 0.05 to

Table 1. Initial rates (k_i), pseudo first order rate constants (k') and second order rate constants (k) in the reaction of Sulfanilic Acid with Chloramine-T in acid perchlorate medium $[HClO_4] = 0.1 \text{ mol dm}^{-3}$, 30°C

$10^3[SA]$ mol dm^{-3}	$10^3[CAT]$ mol dm^{-3}	$10^6(k_i)$ $\text{mol dm}^{-3} \text{ s}^{-1}$	$10^4(k')$ s^{-1}	$10^2(k)$ $\text{dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
5.0	1.0	0.4	–	7.7 (7.6)
5.0	2.0	0.8	–	7.7 (7.7)
5.0	3.0	1.2	–	7.7 (7.8)
5.0	4.0	1.5	–	7.7 (7.7)
5.0	5.0	1.9	–	7.7 (7.7)
10	1.0	0.8	–	7.7 (7.7)
10	2.0	1.5	–	7.7 (7.7)
10	3.0	2.3	–	7.7 (7.8)
10	4.0	3.1	–	7.7 (7.7)
10	5.0	3.8	–	7.7 (7.7)
11	0.5	–	8.4	(7.7)
11	0.75	–	8.4	(7.7)
11	1.0	–	8.6	(7.8)
11	1.5	–	8.6	(7.8)
11	2.0	–	8.6	(7.8)
2.0	2.0	0.3	–	7.7 (7.5)
3.0	2.0	0.5	–	7.7 (7.8)
4.0	2.0	0.6	–	7.7 (7.9)
6.0	2.0	0.9	–	7.7 (7.8)
8.0	2.0	1.2	–	7.7 (7.7)
10	2.0	1.5	–	7.7 (7.7)
2.0	3.0	0.5	–	7.7 (7.8)
3.0	3.0	0.7	–	7.7 (7.8)
4.0	3.0	0.9	–	7.7 (7.8)
5.0	3.0	1.2	–	7.7 (7.8)
6.0	3.0	1.4	–	7.7 (7.8)
7.0	3.0	1.6	–	7.7 (7.6)
8.0	3.0	1.9	–	7.7 (7.8)
9.0	3.0	2.1	–	7.7 (7.7)
10	3.0	2.3	–	7.7 (7.8)
6.0	1.0	–	4.2	(7.1)
8.0	1.0	–	6.2	(7.7)
11	1.0	–	8.5	(7.7)
17	1.0	–	13.0	(7.6)
21	1.0	–	16.0	(7.6)
24	1.0	–	18.3	(7.6)
27	1.0	–	20.2	(7.5)
11	2.0	–	8.6	(7.8)
15	2.0	–	11.5	(7.7)
17	2.0	–	12.9	(7.6)
21	2.0	–	16.0	(7.6)
24	2.0	–	18.2	(7.6)
27	2.0	–	20.1	(7.5)

Figures in parentheses were calculated from pseudo first order rate constants.

0.2 mol dm^{-3} at fixed concentrations of other reaction ingredients viz. $[SA] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[CAT] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[I] = 0.5 \text{ mol dm}^{-3}$ (ionic strength (I) was adjusted by employing lithium perchlorate) at 30° , 35° and 40°C respectively. The rate of the reaction decreases with

increasing hydrogen ion concentration.

Effect of Ionic Strength (I). The effect of ionic strength (I) was studied by employing lithium perchlorate at fixed concentrations of reaction ingredients viz. [SA] = 4.0×10^{-3} mol dm⁻³; [CAT] = 20×10^{-3} mol dm⁻³ and [H⁺] = 0.1 mol dm⁻³ at 30 °C. The rate of the reaction remains unchanged with the changing concentration of LiClO₄ or ionic strength.

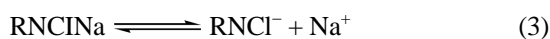
Ruthenium(III) Ion Dependence. Since certain reactions of chloramine-T in acid medium are reportedly catalyzed by RuCl₃. Therefore, it was proper to find out the effect of Ru(III) as a catalyst in this reaction too. The concentration of Ru(III) was varied from 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ at fixed concentrations of other reaction ingredients viz. [SA] = 4.0×10^{-2} mol dm⁻³; [CAT] = 2.0×10^{-3} mol dm⁻³ and [H⁺] = 0.1 mol dm⁻³ at 30°, 40° and 50 °C respectively. However, rate remains unchanged with the changing concentration of the catalyst. Ruling out ruthenium(III) to be a catalyst in this reaction.

Effect of Temperature. The effect of temperature was studied at 30 °C, 35 °C and 40 °C respectively at constant concentrations of other reaction ingredients viz. [SA] = 4.0×10^{-2} mol dm⁻³; [CAT] = 2.0×10^{-3} mol dm⁻³; [H⁺] = 0.1 mol dm⁻³ and [I] = 0.5 mol dm⁻³. The activation parameters such as energy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were evaluated by employing Eyring equation⁴² {ln(k/T) versus 1/T}. The energy and entropy of activation were calculated to be (61.67 ± 0.47) kJ mol⁻¹ and (-62.71 ± 2.48) JK⁻¹mol⁻¹ respectively.

Test of Free Radicals. There appears no possibility of formation of free radicals in this reaction in the light of two-equivalent nature of both chloramine-T and sulfanilic acid. Since no intermediate in one-equivalent reduction of chloramine-T is, yet, known. The addition of acrylic acid as a monomer to polymer does not occur in the reaction. It was observed that acrylic acid does not undergo any polymerization as no white sediment was obtained even on standing the reaction mixture for more than 2-3 h.

Discussion

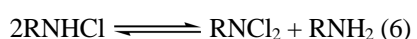
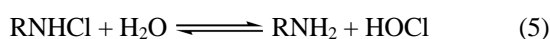
Chloramine-T known to be sodium salt of *N*-chloro-*p*-toluene sulfonamide is considered to be a strong oxidizing as well as chlorinating reagent in aqueous solutions. Such a sodium salt dissociates⁴³ in solution as represented by Eq. (3)



Where R = CH₃-C₆H₄SO₂-

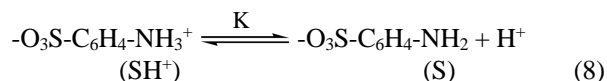
RNCl⁻ is the predominant species of chloramine-T in basic medium.

However, acid dependent species of chloramine-T are governed by the following equilibria⁴⁴ (4)-(7)



Since *p*-toluene sulfonamide (RNH₂) does not affect the rate of the reaction, the reactivity of HOCl and RNCl₂ respectively is ruled out. Also, observed order with respect to chloramine-T is one where as RNCl₂ to be the reactive form accounts for second order with respect to chloramine-T, RNCl₂ to be an active form is further ruled out. OCl⁻ species is reactive in basic medium and such a species cannot be considered to be an active form in acid medium. Therefore, if these facts are taken into account, RNHCl in all probability, appears to be the only reactive form of chloramine-T (henceforth written as CAT) in the title reaction.

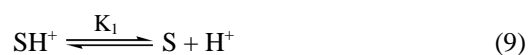
The amino groups of sulfanilic acid exist in aqueous acidic solution is predominantly in protonated form and is governed by equilibrium (8)



Where (SH⁺) and (S) are protonated and molecular forms of sulfanilic acid respectively.

Sulfanilic acid owing to the presence of a free electron pair on the nitrogen of amino group is a good nucleophilic agent. However, -SO₃H group being electron withdrawing reduces its nucleophilicity considerably. The reactions of sulfanilic acid as nucleophile due to the protonation of the amino group should exhibit hydrogen ion dependence in its reactions more particularly reducing the rate of reactions in its redox systems. Since pK_a of sulfanilic acid as reported⁴⁵ earlier was considered unreliable.⁴⁶ The calculations of the concentration of protonated form of the sulfanilic acid. Under such a situation does not appear to be useful analytically.

The kinetic order with respect to the oxidant and substrate is one each and the rate is retarded by hydrogen ion concentration, RNHCl and neutral form of sulfanilic acid (S) are the reactive species of chloramine-T and organic acid respectively to account for these observations. Considering such experimental observations, a plausible reaction mechanism consisting of steps (9)-(11) can be envisaged as follows:



The formation of an adduct in step (II) provides an energetically more facile path, the formation of such an adduct does not appear to be a unique. Since the rate is not affected by ionic strength, such an effect is in line of the proposed mechanism.

The loss of CAT thus leads to the rate law (12)

$$-\frac{d[\text{CAT}]}{dt} = \frac{k'K'K_1[\text{RNHCl}][\text{SA}]}{K_1 + [\text{H}^+]} \quad (12)$$

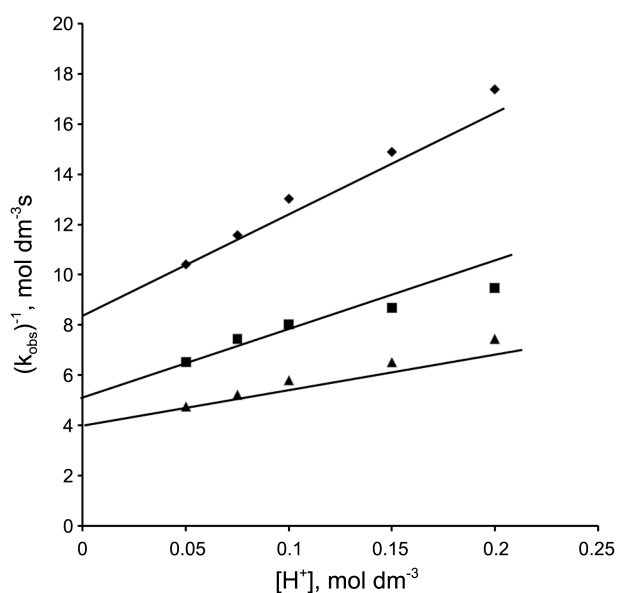


Figure 4. Plots of $(k_{\text{obs}})^{-1}$ versus $[\text{H}^+]$ in the reaction of CAT and sulfanilic acid. $[\text{CAT}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{SA}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$; \blacklozenge 30°, \blacksquare 35° and \blacktriangle 40 °C.

Where $[\text{RNHCl}]$ and $[\text{SA}]$ are the gross analytical concentrations of chloramine-T and sulfanilic acid respectively. Since 'K' is insignificant equilibrium, Eqn. (12) is reduced to Eqn. (13) or (14)

$$-\frac{d[\text{CAT}]}{dt} = \frac{kK_1[\text{RNHCl}][\text{SA}]}{K_1 + [\text{H}^+]} \quad (13)$$

where $k'K' = k$

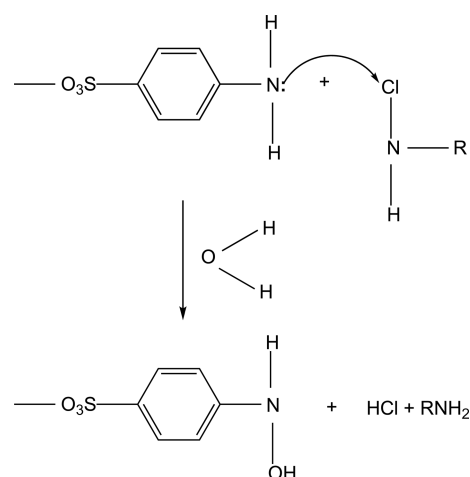
$$\text{or} \quad k_{\text{obs}} = kK_1/(K_1 + [\text{H}^+]) \quad (14)$$

Where k_{obs} is observed second order rate constant (Table 1). Further, the double reciprocal form of Eqn. (14) yields Eqn. (15)

$$\begin{aligned} \frac{1}{k_{\text{obs}}} &= \frac{K_1}{kK_1} + \frac{[\text{H}^+]}{kK_1} \\ &= \frac{1}{k} + \frac{[\text{H}^+]}{kK_1} \end{aligned} \quad (15)$$

A plot of $(1/k_{\text{obs}})$ versus $[\text{H}^+]$ was made from Eqn. (15) that yielded a straight line with non zero intercept (Fig. 4) 'k' was calculated from the intercept to be $(12 \pm 0.1) \times 10^{-3}$, $(18.8 \pm 0.1) \times 10^{-3}$ and $(25 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ at 30, 35 and 40 °C respectively and at $I = 1.0 \text{ mol dm}^{-3}$. 'K₁' was calculated from the ratio of the intercept and slope to be (0.22 ± 0.01) , (0.32 ± 0.02) and $(0.45 \pm 0.02) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 30, 35 and 40 °C respectively and at $I = 1.0 \text{ mol dm}^{-3}$. K₁ being significantly small conforms to much weaker adduct formation between oxidant and substrate under experimental conditions.

So far the mode of electron transfer from substrate to the oxidant is concerned, following Scheme 1 can tentatively account for the reaction events.



The large negative value of the entropy of activation is in line of the bimolecular type mechanism and account for an orientation of transition state and solvation of the activated complex. Since the size of the substrate is significantly large, this more negative entropy can be assigned to it as suggested earlier.⁴⁷

Conclusion

In conclusion, an interaction between chloramine-T and sulfanilic acid in acid aqueous medium is second order; the rate is retarded by hydrogen ion. A mechanism based on an adduct formation has been considered to account for the reaction mechanism. Also, the speciation of chloramines-T species is discussed in detail and the most probable species has been identified for oxidation of sulfanilic acid.

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