

Kinetic and mechanistic study of bromination of sulfanilic acid with *N*-bromosuccinimide in alkaline medium

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Received November 23, 2010, Revised April 22, 2010

The sulfanilic acid (*p*-amino benzene sulfonic acid) (SNA) is an important and interesting compound which finds a number of applications in the syntheses of organic dyes. The amide of sulfanilic acid (sulfanilamide) and certain related substituted amides are of considerable medicinal importance as the sulfa drugs. The kinetics of bromination of SNA with *N*-bromosuccinimide (NBS) in NaOH medium has been studied at 308 K. The experimental rate law obtained is $-d[NBS]/dt = [NBS][SNA]^x[OH^-]$ where *x* is less than unity. The reaction was subjected to changes in concentration of succinimide, the reduction product of NBS, concentration of added neutral salt, as well as to dielectric permittivity and ionic strength of the medium. Solvent isotope effect has been studied using D₂O. The stoichiometry of the reaction has been determined, and the products were identified and characterized. Activation parameters for the overall reactions have been computed using the Arrhenius plot. OBr⁻ has been postulated as the reactive species of NBS. The reaction fails to induce polymerization of added acrylonitrile. The proposed mechanism and the derived rate law are consistent with the observed kinetic data.

Key words: *N*-bromosuccinimide, sulfanilic acid, bromination, alkaline medium.

INTRODUCTION

The Sulfanilic acid (*p*-aminobenzene sulfonic acid) (SNA) is an important and interesting compound, which finds a number of applications in the syntheses of organic dyes [1]. The amide of sulfanilic acid (sulfanilamide) and certain related substituted amides are of considerable medicinal importance as the sulfa drugs. Although they have been supplanted to a wide extent by antibiotics such as penicillin, terramycin, chloromycetin, and aureomycin, the sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical industry [2]. The kinetics of ruthenium (III) catalysed oxidation of sulfanilic acid by hexacyanoferrate(III) in alkaline medium has been studied [3]. In view of this, it becomes important to study sulfanilic acid because of its biological importance and reactivity towards different oxidants. *N*-bromosuccinimide (NBS) is a source of positive halogen, and this reagent has been exploited as an oxidant for a variety of substrates [4-8] in both acidic and alkaline solutions. The use of NBS as an oxidant is extensive in the determination of number of organic compounds [9-12]. However, a little information exists in the literature on NBS reactions, particularly with respect to the oxidation

kinetics of pharmaceuticals [13, 14], which may throw some light on the mechanism [15] of the metabolic conversions in the biological systems. In view of these facts, there is a considerable scope for the study of the reactions with NBS to get better insight of the speciation of NBS reaction models and to understand its redox chemistry in solutions. This paper reports for the first time on the detailed kinetics of SNA bromination with NBS in NaOH medium. The work was carried out with the intention to elucidate the mechanism of the reaction, to put forward the appropriate rate law, to identify the products of the reaction, and to ascertain the reactive species of NBS.

EXPERIMENTAL

Materials

An aqueous solution of NBS was prepared afresh each day from a G.R. Merck sample of the reagent, and its strength was checked by the iodometric method. Sulfanilic acid (Merck) is not only insoluble in organic solvents, but also nearly insoluble in water and in aqueous acids. Sulfanilic acid is soluble in aqueous bases. Therefore the solution of sulfanilic acid was prepared by dissolving an appropriate amount of the sample in warm very dilute alkaline solution. All other reagents, namely sodium hydroxide, sodium perchlorate and succinimide, were of Analar grade.

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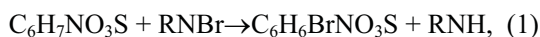
Doubly distilled water was used throughout the investigations.

Kinetic measurements

All kinetic measurements were performed in glass stoppered Pyrex boiling tubes coated black to eliminate the photochemical effects. The reactions were carried out under pseudo-first-order conditions by taking a known excess of $[SNA]_0$ over $[NBS]_0$ at 308 K. Appropriate amounts of SNA, NaOH solutions, sodium perchlorate, and water to keep the total volume constant were equilibrated at constant temperature ($\pm 0.1^\circ\text{C}$). A measured amount of NBS solution also pre-equilibrated at the same temperature was rapidly added to the mixture. The progress of the reaction was monitored by estimating the amount of unconsumed NBS at regular time intervals iodometrically. The course of reaction was studied for at least two half-lives. The pseudo-first-order rate constants (k_{obs}), calculated from the linear plots of $\log [NBS]$ vs. time were reproducible within $\pm 4\%$. Regression analysis of the experimental data to obtain regression coefficient, r was performed using MS Excel.

Stoichiometry and product analysis

Reaction mixtures, containing varying ratios of NBS and SNA in the presence of 0.01 mol dm^{-3} NaOH at 308 K, were kept aside for 48 h, so that the substrate was completely converted into products. Estimation of the unreacted NBS showed that one mole of substrate utilized one mole of NBS, confirming the following stoichiometry:



where $\text{R} = (\text{CH}_2\text{CO})_2$.

The products in the reaction mixture were extracted with ether. The combined ether extract was evaporated and subjected to column chromatography on silicagel. The reduction product of NBS, succinimide (RNH), was detected by spot tests [16] and confirmed by IR absorption bands, as follows RNH: A broad band at 3450 cm^{-1} for NH stretching mode and a sharp band at 1698 cm^{-1} for $\text{C} = \text{O}$ stretching mode. The bromination product of sulfanilic acid was found to be 4-amino 3-bromo benzene sulfonic acid and identified by its IR absorption bands: 3030 cm^{-1} (Aromatic C-H stretch), 3226 cm^{-1} (N-H stretch), 1275 cm^{-1} (C-N stretch) and 588 cm^{-1} (C-Br stretch). Further, it was confirmed by ^1H NMR spectral studies: ^1H NMR (DMSO- d_6 , 400 MHz) δ : 9.74 (s, 1H, OH), 7.85 (s, 1H, Ar-H), 7.62 (d, 1H, Ar-H), 6.63 (d, 1H, Ar-H), 7.62 (s, 2H, NH_2). IR spectrum was recorded on FT-IR spectrometer using KBr pellets. ^1H NMR

spectrum was recorded on Shimadzu AMX 400-Bruker, 400MHz spectrometer using DMSO as a solvent and TMS as internal standard.

RESULTS

The bromination of SNA with NBS was kinetically investigated at several initial concentrations of the reactants in NaOH medium at 308 K. The salient feature obtained in this medium is discussed as follows.

The effect of varying reactant concentrations on the rate

Under pseudo-first-order conditions ($[SNA] \gg [NBS]$) at constant $[\text{NaOH}]$ and temperature, the plots of $\log [NBS]$ vs. time were linear ($r \geq 0.997$), indicating a first-order dependence of the rate on $[NBS]_0$. Table 1 gives the calculated pseudo-first-order rate constants (k_{obs}). Further, the values of k_{obs} calculated from these plots are unaltered with $[NBS]_0$ variation, confirming the first-order dependence on $[NBS]_0$. The rate increased with the $[SNA]_0$ increase (Table 1). A plot of $\log k_{\text{obs}}$ vs. $\log [SNA]$ was linear (Fig. 1; $r = 0.999$) with a slope of 0.72, indicating a fractional-order dependence of the rate on $[SNA]_0$.

Table 1. The effect of varying concentrations of NBS, SNA and NaOH on the reaction rate at 308 K. Ionic strength - $\mu = 0.1 \text{ mol dm}^{-3}$; a - at $\mu = 0.15 \text{ mol dm}^{-3}$; b - at $\mu = 0.25 \text{ mol dm}^{-3}$

$[NBS] \times 10^4$ mol dm^{-3}	$[SNA] \times 10^3$ mol dm^{-3}	$[\text{NaOH}] \times 10^3$ mol dm^{-3}	$k_{\text{obs}} \times 10^4$ s^{-1}
1.0	8.0	10.0	4.15
3.0	8.0	10.0	4.18
5.0	8.0	10.0	4.10
7.0	8.0	10.0	4.12
9.0	8.0	10.0	4.17
5.0	4.0	10.0	2.42
5.0	6.0	10.0	3.31
5.0	10.0	10.0	4.68
5.0	12.0	10.0	5.49
5.0	8.0	6.0	2.29
5.0	8.0	8.0	3.22
5.0	8.0	12.0	5.02
5.0	8.0	14.0	5.86
^a 5.0	8.0	10.0	4.16
^b 5.0	8.0	10.0	4.19

The effect of varying $[\text{NaOH}]$ on the rate

The rate increased with the increase in $[\text{NaOH}]$ (Table 1). A plot of $\log k_{\text{obs}}$ vs. $\log [\text{NaOH}]$ was linear (Fig. 2; $r = 0.998$) with a slope of 1.03, indicating a first-order dependence of the rate on $[\text{NaOH}]$.

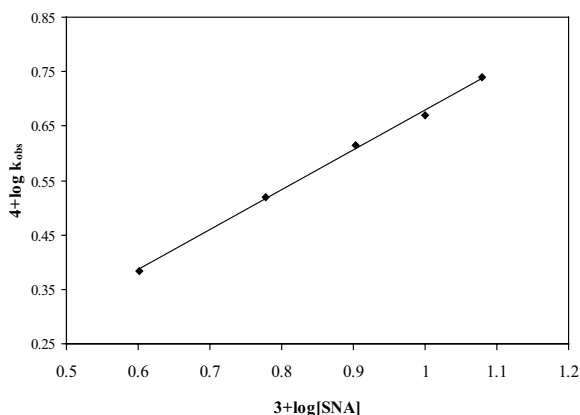


Fig. 1: Plot of $4 + \log k_{\text{obs}}$ vs. $3 + \log [\text{SNA}]$.

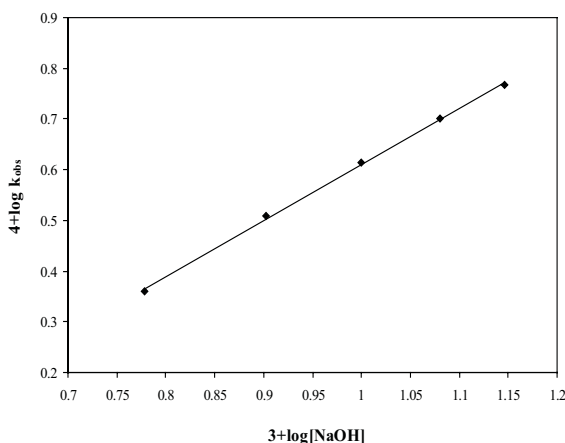


Fig. 2: Plot of $4 + \log k_{\text{obs}}$ vs. $3 + \log [\text{NaOH}]$.

The effect of added product

The effect of initially added product, succinimide (RNH) was studied in the concentration range from 0.0002 to 0.001 mol dm⁻³, keeping all other concentrations constant. It was found that the added product had no significant effect on the reaction rate.

The effect of the dielectric permittivity (D) and the ionic strength (μ) of the medium

The effect of the dielectric permittivity (D) on the reaction rate was studied by adding various proportions of CH₃CN (0 - 20 % v/v) to the reacting system. The rate decreased with increasing CH₃CN content and the results are shown in Table 2.

The plot of $\log k_{\text{obs}}$ vs. $1/D$ was linear ($r = 0.997$) with a negative slope. The values of permittivity (D) for the CH₃CN-H₂O mixtures are calculated through the equation, $D = D_w V_w + D_A V_A$ where D_w and D_A are the dielectric permittivities of pure water and acetonitrile, and V_w and V_A are the volume fractions of components, water and acetonitrile in the total mixture. Blank experiments

Table 2. The effect of varying dielectric permittivity of the medium on the reaction rate at 308 K

% CH ₃ CN (v/v)	D	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
0	73.6	4.10
5	71.8	3.22
10	70.0	2.34
15	68.2	1.96
20	66.5	1.88

[NBS] = 5×10^{-4} mol dm⁻³; [SNA] = 8×10^{-3} mol dm⁻³; [NaOH] = 10×10^{-3} mol dm⁻³; $\mu = 0.1$ mol dm⁻³.

performed indicated that CH₃CN was not oxidized with NBS under the experimental conditions employed. Variation of ionic strength of the medium (0.1-0.3 mol dm⁻³) using NaClO₄ solution had no significant effect on the rate.

Solvent isotope effect and proton inventory studies

Solvent isotope study in D₂O medium was made. The value of k_{obs} (H₂O) is 4.10 and that of the k_{obs} (D₂O) is 2.33 leading to solvent isotope effect k_{obs} (H₂O) / k_{obs} (D₂O) = 1.73. Proton inventory studies were made in H₂O - D₂O mixtures, and the results are shown in Table 3. The corresponding proton inventory plot for the rate constant, k_{obs} in a solvent mixture containing deuterium atom fraction (n) is given in Fig. 3.

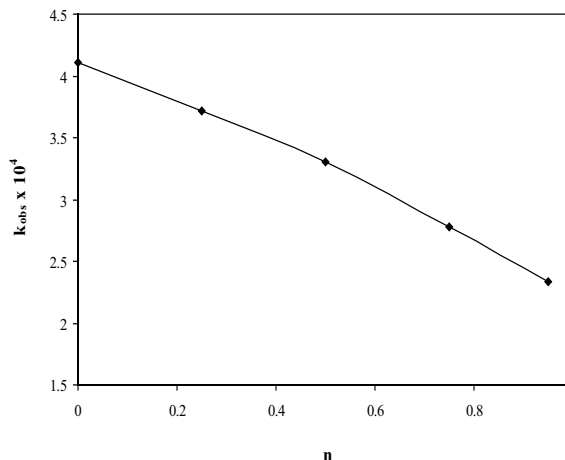


Fig. 3: Plot of k_{obs} vs. n.

Table 3. Proton inventory studies in H₂O - D₂O mixture at 308 K

Atom fraction of D ₂ O (n)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
0.00	4.10
0.25	3.71
0.50	3.30
0.75	2.78
0.95	2.33

[NBS] = 5×10^{-4} mol dm⁻³; [SNA] = 8×10^{-3} mol dm⁻³; [NaOH] = 10×10^{-3} mol dm⁻³; $\mu = 0.1$ mol dm⁻³.

The Effect of Temperature

Kinetic and thermodynamic parameters were calculated by studying the reaction at different temperatures (303 – 321 K). The results are given in Table 4. The values of activation parameters for the overall reaction were computed through the linear Arrhenius plot of $k_{\text{obs}} \log$ vs. $1/T$ (Fig. 4; $r = 0.997$). The results are compiled in Table 5.

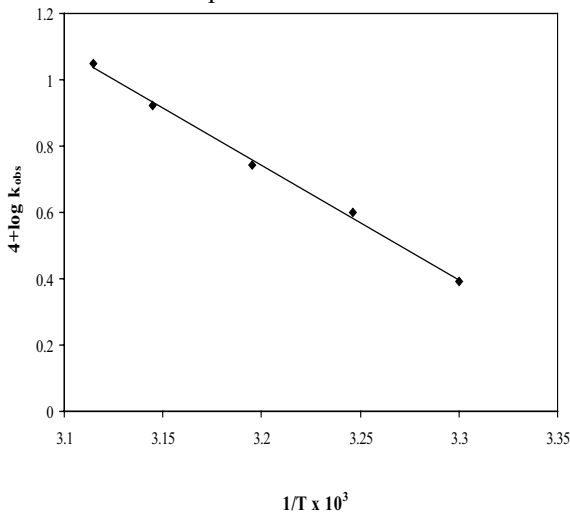


Fig. 4: Plot of $4 + \log k_{\text{obs}}$ vs. $10^3/T$.

Table 4. The effect of varying temperature on the reaction rate

Temperature, K	$k_{\text{obs}} \times 10^4, \text{s}^{-1}$
303	2.45
308	4.10
313	5.52
318	8.37
321	11.24

$[\text{NBS}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{SNA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{NaOH}] = 10 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$.

Table 5. Activation parameters for the bromination of SNA

E_a kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹
57.83	55.20	96.10	-130.84

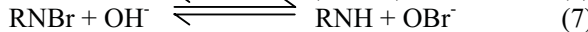
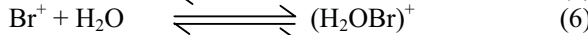
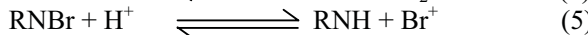
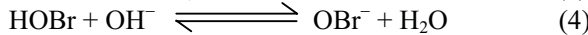
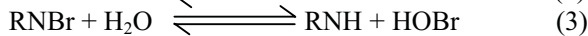
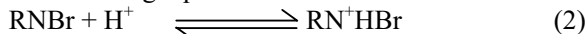
Test for Free Radicals

Addition of aqueous acrylonitrile monomer solution to the reaction mixture in an inert atmosphere did not initiate polymerization, indicating the absence of free radical species in the reaction sequence.

DISCUSSION AND MECHANISM

NBS is a two equivalent oxidant which oxidizes many substrates through NBS itself or Br^+ or RN^+HBr or hypobromite anion. The reactive species responsible for brominating character may

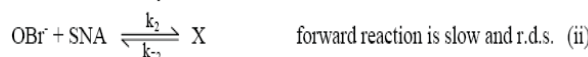
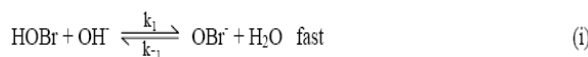
depend on the pH of the medium [6]. Depending on the pH of the medium NBS furnishes different types of reactive species in solutions [17-19] as shown in the following equilibria:



where R is $(\text{CH}_2\text{CO})_2$.

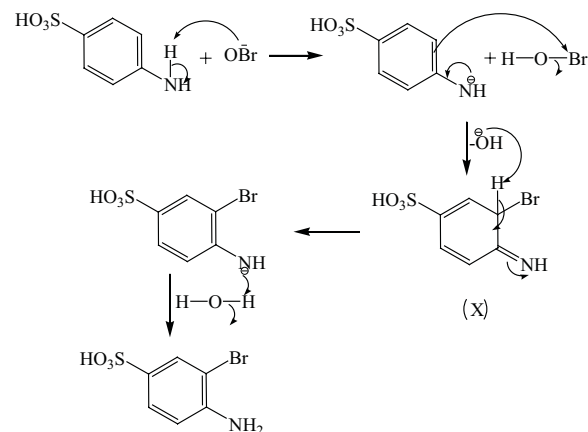
In acid medium, the probable reactive species of NBS are NBS itself or Br^+ or protonated NBS (RN^+HBr), and the reactive species in alkaline solutions are NBS itself HOBr or OBr^- .

NBS oxidizes many substrates through NBS itself, or hypobromite anion [20, 21]. In this study, the reaction exhibits 1:1 stoichiometry of SNA and NBS with unit order dependence on $[\text{NBS}]$. The increase in rate with increasing $[\text{OH}^-]$ can be well-explained [22] by the formation of OBr^- according to equilibria (4) and (7). The insignificant effect of added succinimide on the rate can be attributed to the involvement of OBr^- according to the equilibrium step (4). Hence, OBr^- reacts with the substrate to form a complex (X) in the rate determining step, which then undergoes rearrangement in the fast step to give products as shown in Scheme 1.



Scheme 1

A detailed mechanistic interpretation is shown in Scheme 2.



Scheme 2

From slow step of Scheme 1,

$$\text{rate} = k_2 [\text{OBr}^-] [\text{SNA}] \quad (8)$$

Applying steady state condition for OBr^-

$$k_1[\text{HOBr}][\text{OH}^-] - k_{-1}[\text{OBr}^-][\text{H}_2\text{O}] - k_2[\text{OBr}^-][\text{SNA}] = 0$$

$$[\text{OBr}^-] \{k_{-1}[\text{H}_2\text{O}] + k_2[\text{SNA}]\} = k_1[\text{HOBr}][\text{OH}^-]$$

$$[\text{OBr}^-] = \frac{k_1[\text{HOBr}][\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2[\text{SNA}]} \quad (9)$$

By inserting $[\text{OBr}^-]$ from Eq.(9) into Eq.(8) the following rate law (Eq.10) is obtained:

$$\text{rate} = \frac{k_1 k_2 [\text{NBS}][\text{OH}^-][\text{SNA}]}{k_{-1}[\text{H}_2\text{O}] + k_2[\text{SNA}]} \quad (10)$$

Since $\text{rate} = k_{\text{obs}} [\text{NBS}]$, Eq.(10) can be transformed into Equations (11) and (12).

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{OH}^-][\text{SNA}]}{k_{-1}[\text{H}_2\text{O}] + k_2[\text{SNA}]} \quad (11)$$

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}[\text{H}_2\text{O}]}{k_1 k_2 [\text{OH}^-][\text{SNA}]} + \frac{1}{k_1 [\text{OH}^-]} \quad (12)$$

Based on Eq. (12), a plot of $1/k_{\text{obs}}$ vs. $1/[\text{SNA}]$ was found to be linear (Fig. 5; $r = 0.998$). From the intercept and slope of the plot, the values of k_1 and k_{-1}/k_2 at standard $[\text{OH}^-]$ and $[\text{H}_2\text{O}] = 55.56 \text{ mol dm}^{-3}$, were found to be $0.1371 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and 3.3703×10^{-4} , respectively. The proposed Scheme 1 and the rate law are also substantiated by the experimental results, discussed below.

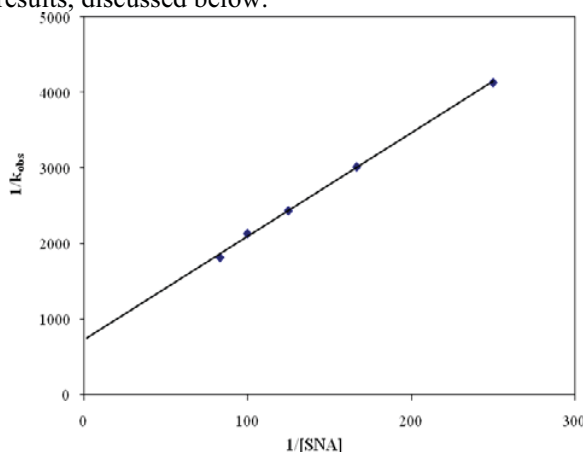


Fig. 5: Plot of $1/k_{\text{obs}}$ vs. $1/[\text{SNA}]$.

The change in solvent composition by varying the CH_3CN content into $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture affects the reaction rate. For a limiting case of zero angle of approach between the two dipoles or a ion - dipole system, Amis [23] showed that a plot of $\log k_{\text{obs}}$ vs. $1/D$ gives a straight line with a positive slope for a reaction between a positive ion-dipole interaction, whereas a negative slope for a reaction between a

negative ion and a dipole or between two dipoles. In this investigation, a plot of $\log k_{\text{obs}}$ vs. $1/D$ was linear with a negative slope. This observation indicates the ion-dipole nature of the rate determining step in the reaction sequence and also points to extending of charge to the transition state.

The observed solvent isotope effect supports the proposed mechanism and the derived rate law. For a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O medium, since D_3O^+ and OD^- are stronger acid and stronger base, respectively than H_3O^+ and OH^- ions [24, 25]. In the present case, the observed solvent isotope effect of $k_{\text{obs}}(\text{H}_2\text{O}) / k_{\text{obs}}(\text{D}_2\text{O}) > 1$ is due to the protonation step followed by hydrolysis involving the OH bond scission. The retardation of rate in D_2O is due to the hydrolysis step which tends to make the normal kinetic isotope effect. The proton inventory studies made in $\text{H}_2\text{O} - \text{D}_2\text{O}$ mixture could throw light on the nature of the transition state. The dependence of the rate constant, k_{obs} , on the deuterium atom fraction 'n' in the solvent mixture is given by the following form of Gross-Butler equation [26],

$$\frac{k_o^1}{k_n^1} = \frac{\pi \text{TS}(1 - n + n\phi_i)}{\pi \text{RS}(1 - n + n\phi_j)} \quad (13)$$

where ϕ_i and ϕ_j are isotope fractionation factor for isotopically exchangeable hydrogen sites in the transition state (TS) and in the ground / reactant state (RS), respectively. The Gross-Butler equation permits the evaluation of ϕ_i when the value of ϕ_j is known. However, the curvature of proton inventory plot could reflect the number of exchangeable proton in the reaction [26]. Plot of k_{obs} vs. n is a curve in this case, and this in comparison with the standard curves indicates the involvement of a single proton or H-D exchange in the reaction sequence [27]. This proton exchange is indicative of the participation of hydrogen in the formation of transition state.

The negligible influence of added succinimide and halide ions on the rate are in agreement with the proposed mechanism. The proposed mechanism is also supported by the high values of energy of activation and other thermodynamic parameters. The fairly high positive value of ΔH^\ddagger indicates that, the transition state is highly solvated.

CONCLUSIONS

In conclusion, the stoichiometry of bromination of SNA by NBS is 1:1. The bromination product of SNA was found to be 4-amino-3-bromobenzene sulfonic acid, and confirmed by IR and ^1H NMR spectral studies. OBr^- is postulated as the reactive species of NBS. Solvent isotope effect, studied using

D₂O, supports the proposed mechanism, and the derived rate law is consistent with the observed results.

Acknowledgement: The authors are thankful to the University of Mysore, Mysore, India for the financial support.

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КИНЕТИЧНО И МЕХАНИСТИЧНО ИЗСЛЕДВАНЕ НА БРОМИРАНЕТО НА СУЛФАНИЛОВА КИСЕЛИНА С *N*-БРОМО-СУКЦИНИМИД В АЛКАЛНА СРЕДА

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Постъпила на 23 ноември 2009 г.; преработена на 22 април 2010 г.

(Резюме)

Сулфаниловата киселина (*p*-амино бензен-сулфонова киселина, SNA) е важно и интересно съединение, което намира редица приложения при синтезите на органични багрила. Нейният амид (сулфаниламидът) и някои подобни субституирани амиди са със значително приложение в медицината като лекарства. В настоящата работа е изследвана кинетиката на бромирането на SNA с *N*-бромосукцинимид (NBS) при 308 K в алкална среда от натриева основа. Експериментално е изведено следното кинетично уравнение: $-d[NBS]/dt = [NBS][SNA]^2[OH^-]$, от дробен порядък по отношение на SNA. Изследвани са измененията на концентрациите на сукцинимида, на продуктите на редукцията на NBS, на добавяната неутрална сол, както и диелектричната проникваемост и йонната сила на средата. Изотопният ефект на разтворителя е изследван с помощта на D₂O. Определена е стехиометрията на реакцията, а продуктите ѝ са идентифицирани и охарактеризирани. Параметрите на активация за сумарните реакции са изчислени чрез координатите на Арениус. Постулирано е, че йонът OBr⁻ е реактивоспособната частица за NBS. При добавянето на акрилонитрил не се наблюдава полимеризация. Предложеният механизъм и изведеното кинетично уравнение са в съгласие с получените кинетични данни.