

MECHANISTIC INVESTIGATIONS WITH POSITIVE HALOGENS: KINETICS OF  
OXIDATION OF THIOSEMICARBAZIDE BY CHLORAMINE-B, BROMAMINE-B  
AND DICHLORAMINE-B IN ACID MEDIUM.

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(Received in UK 9 March 1987)

**Abstract** - Kinetics of oxidation of thiosemicarbazide (TSC) by chloramine-B (CAB), and bromamine-B (BAB) in aqueous perchloric acid medium and by dichloramine-B (DCB) in 1:1 (v/v) water - methanol medium has been studied. The rate followed first order kinetics in [oxidant] and inverse fractional order in [H<sup>+</sup>] with all the oxidants. But it was fractional order in [TSC] with CAB and independent of [TSC] with BAB and DCB. Addition of benzenesulphonamide, the reduced product of the oxidants had no effect on the rate with CAB and BAB but it slightly increased the rate with DCB. The rate decreased with increase in ionic strength of the medium in all cases. Decrease of dielectric constant of the reaction medium by adding methanol had no effect on the rate with CAB and BAB but increased the rate with DCB. The mechanisms proposed and the derived rate laws are in conformity with the observed results. The coefficients of the rate limiting steps have been calculated. Kinetics observed with HOCl and HOBr support the proposed mechanisms.

INTRODUCTION

The chemistry of thiosemicarbazide (TSC) and its derivatives, thiosemicarbazones, has attracted the attention of many investigators due to their biological activity and applications<sup>1,2</sup>. They are very good metal chelating agents and find applications in the characterization of aldehydes, ketones and polysaccharides. They are antitubercular active and also active against influenza, protozoa, small pox and certain kinds of tumour. They are also possible pesticides and fungicides.

Although the N-haloaromatic sulphonamides have been extensively used for determining TSC in the pure state and in its metal complexes<sup>3</sup>, there are no reports on the mechanistic aspects of TSC and N-halosulphonamide reactions. The present investigation is a part of our kinetic and mechanistic studies with positive halogens<sup>4-7</sup>. We report herein the kinetics of oxidation of TSC by chloramine-B (CAB) and bromamine-B (BAB) in aqueous media and dichloramine-B in 1:1 (v/v) aqueous methanol.

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## MATERIALS AND METHODS

Chloramine-B (CAB, Sodium N-Chloro-benzenesulphonamide) was prepared by the partial chlorination of benzenesulphonamide (BSA)<sup>8</sup>. Bromamine-B (Sodium N-bromo-benzenesulphonamide, BAB) was obtained by the partial debromination of dibromamine-B<sup>9</sup>. Dichloramine-B (N, N-dichlorobenzene sulphonamide, DCB) was prepared by the chlorination of chloramine-B<sup>10</sup>. The purity of the oxidants, CAB, BAB and DCB was checked by recording their spectra and estimating the amount of active halogen present in them. Aqueous stock solutions (0.1 mol dm<sup>-3</sup>) of CAB and BAB, and DCB in methanol were prepared, standardised and stored in dark coloured bottles. HOCl and HOBr in solution were prepared by standard methods and standardised by iodometric method.

Thiosemicarbazide (TSC) (E.Merck) was purified by recrystallization from the aqueous solution of the sample. Aqueous stock solutions (0.1 mol dm<sup>-3</sup>) of TSC was prepared. The ionic strength of the reaction medium was kept at 0.5 mol dm<sup>-3</sup> with sodium perchlorate (E.Merck). All other reagents used were of analar grade.

Kinetic Measurements

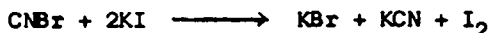
The kinetic studies were made in glass stoppered pyrex boiling tubes under pseudo-first-order conditions were [TSC] > [oxidant] (5 to 20 fold excess). The reactions were initiated by the rapid addition of requisite amounts of oxidant solution, thermally pre-equilibrated at a desired temperature, to a mixture containing known amounts of TSC, perchloric acid and sodium perchlorate solutions and water (and methanol with DCB to maintain 1:1 (v/v) aqueous methanol), pre-equilibrated at the same temperature. The progress of the reactions was monitored for at least two half lives by iodometric determination of unreacted oxidant at regular intervals of time. The pseudo-first-order rate constants ( $k_{obs}$ ) were computed by the method of least squares and were reproducible within  $\pm 3\%$ .

Stoichiometry and Product Analysis

The stoichiometries of TSC-CAB, TSC-BAB and TSC-DCB reactions were determined by allowing the reactions to go to completion at 303 K at different [TSC]/[oxidant] ratios and [H<sup>+</sup>] (0.02-0.2 mol dm<sup>-3</sup>). The products sulphate, cyanate and cyanogen bromide in the reaction mixtures were detected by standard tests<sup>11-13</sup>. The presence of cyanate ion in the reaction products was detected by spot tests<sup>11</sup> and also by Werner's test<sup>12</sup>.

Werner's test : To the reaction product, 0.2 dm<sup>3</sup> each of 20% pyridine and 0.2% Copper Sulphate solutions were added. The resulting solution was agitated with CHCl<sub>3</sub>. Appearance of a blue tint, Cu(OCN)<sub>2</sub>. 2C<sub>6</sub>H<sub>5</sub>N, in the aqueous layer showed the presence of CNO<sup>-</sup> in the reaction products.

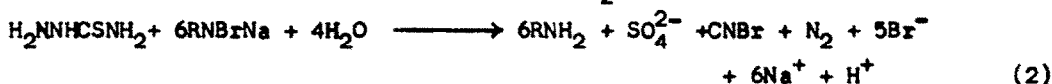
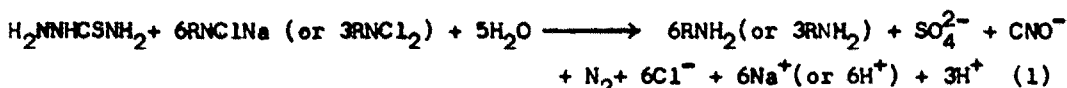
Further cyanogen bromide and sulphate were quantitatively estimated by Schulek's iodometric<sup>14</sup> and gravimetric methods<sup>15</sup> respectively. Cyanogen bromide in the reaction products<sup>3</sup>, after the completion of reaction, was treated with 1.0 dm<sup>3</sup> 2NH<sub>2</sub>SO<sub>4</sub> and 1.0 dm<sup>3</sup> 10% KI solutions. The iodine liberated by the reaction



was titrated against 0.01 N sodium thiosulphate. 93  $\pm$  2% yield of CNBr was obtained.

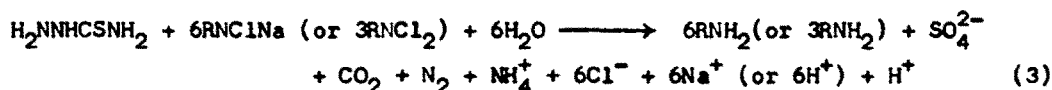
Sulphate in the reaction products was precipitated as BaSO<sub>4</sub> and estimated gravimetrically<sup>15</sup>. The yields were 95  $\pm$  2%.

Benzenesulphonamide (BSA), the reduced product of the oxidants was detected by TLC<sup>16</sup> employing ether-chloroform-n-butanol (2:2:1 v/v) as solvent and iodine as detecting reagent ( $R_f = 0.88$ ). The observed stoichiometries may be represented by equations 1 and 2.



Where R = C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>.

Although the observed 1:6 stoichiometry with CAB and DCB may also be represented by equation 3,



corresponding to the formation of CO<sub>2</sub> and ammonia as products instead of CNO, the former are formed in negligible quantities. Identical 1:6 stoichiometries were observed with both HOCl and HOBr.

### RESULTS

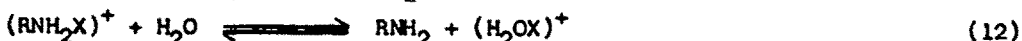
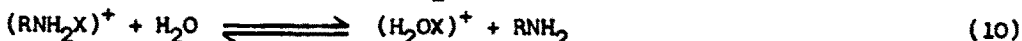
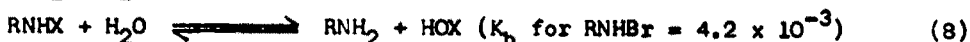
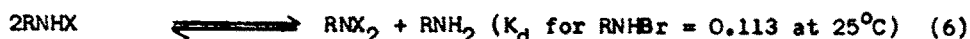
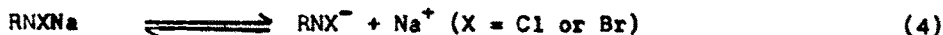
Kinetics of oxidations of TSC by CAB, BAB, DCB, HOCl and HOBr were investigated at several initial concentrations of the reactants and HClO<sub>4</sub> (0.02–0.2 mol dm<sup>-3</sup>) (Tables 1–3 and Fig. 1–2). At constant [acid] with several fold excess of the [substrate] (5–20 times), the plots of log ([oxidant]/[oxidant] versus time were linear for two half lives with all the oxidants and the pseudo-first-order rate constants were unaffected by the change in [oxidant], showing first order kinetics in [oxidant] with all the oxidants. At constant [oxidant] and [TSC] the rates decreased with increase in [HClO<sub>4</sub>] in all cases and the plots of log k<sub>obs</sub> versus log [H<sup>+</sup>]<sub>eff</sub> (Table 1) were linear with varying slopes indicating fractional order in [H<sup>+</sup>] (Table 3). At constant [HClO<sub>4</sub>] and [oxidant] the rates increased with increase in [TSC] with fractional order dependence in the cases of CAB and HOCl and the rate was independent of [TSC] in other cases (Table 3).

The rates decreased slightly with increase in ionic strength of the medium in all cases (Table 2). But the change in dielectric constant of the medium by changing the solvent composition with methanol had no effect on the rate with all the oxidants except DCB. With the latter the rate increased with decrease in dielectric constant of the medium. The plot of log k<sub>obs</sub> versus 1/D was linear with a positive slope. Addition of the reaction products benzenesulphonamide (BSA) and Cl<sup>-</sup> (with CAB) or Br<sup>-</sup> (with BAB) had no effect on the rate with CAB and BAB. With DCB the rate slightly increased with the addition of a small quantity of BSA. But further additions had no significant effect on the rate.

The rates were measured at different temperatures and the activation parameters were computed in all cases.

### DISCUSSION

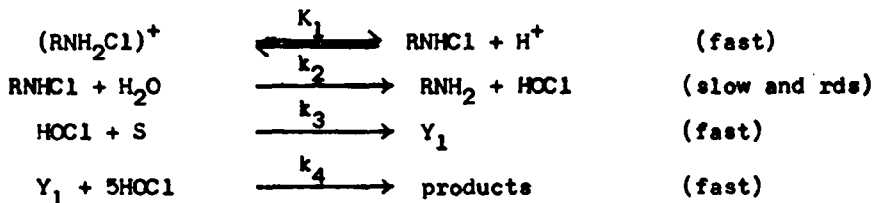
Chloramine-B, like chloramine-T<sup>4,17-19</sup> and bromamine-B<sup>18</sup> are fairly strong electrolytes in aqueous solution and they furnish different reactive species depending upon the pH of the medium. The following equilibria exist in the aqueous or partially aqueous solutions of CAB, BAB and DCB.



Hence the probable oxidising species in acid solutions of the oxidants are  $\text{RNHX}$ ,  $(\text{RNH}_2\text{X})^+$ ,  $\text{HOX}$ ,  $(\text{H}_2\text{OX})^+$  and  $\text{RNX}_2$ . Under the present experimental conditions, at  $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$ , the oxidants are likely to be in the protonated forms,  $(\text{RNH}_2\text{X})^+$  or  $(\text{H}_2\text{OX})^+$ .

#### Mechanism of Oxidations

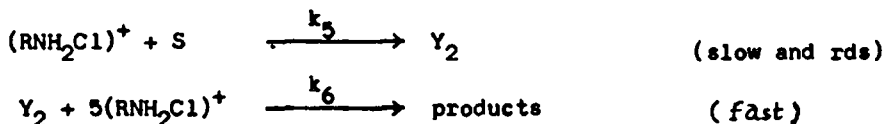
1) With chloramine-B and HOCl : The kinetics of first order in  $[\text{CAB}]$ , fractional order in  $[\text{TSC}]$  and inverse fractional order in  $[\text{H}^+]$  and observed non-influence of the product ( $\text{BSA}$ ,  $\text{RNH}_2$ ) may be explained by two pathway mechanism (Schemes 1 and 2).



#### Scheme - 1

Based on Scheme 1, the rate law (13) has been deduced.

$$-\frac{d[\text{CAB}]}{dt} = \frac{K_1 k_2 [\text{CAB}] [\text{H}_2\text{O}]}{k + [\text{H}^+]}, \text{ where } k = \frac{k_2 [\text{H}_2\text{O}]}{k_{-1}} \quad (13)$$



#### Scheme - 2

The related rate law is given by

$$-\frac{d[\text{CAB}]}{dt} = k_5 [\text{CAB}] [\text{S}] \quad (14)$$

The combined rate law (15) accounts for the observed results,

$$-\frac{d[\text{CAB}]}{dt} = \frac{K_1 k_2 [\text{CAB}] [\text{H}_2\text{O}]}{k + [\text{H}^+]} + k_5 [\text{CAB}] [\text{S}] \quad (15)$$

or

$$k_{\text{obs}} = \frac{K_1 k_2 [\text{H}_2\text{O}]}{k + [\text{H}^+]} + k_5 [\text{S}] \quad (16)$$

predicting a linearity between  $k_{\text{obs}}$  and  $[\text{S}]$ . The plot of  $k_{\text{obs}}$  versus  $[\text{S}]$  was linear (Fig.2) supporting the rate law. The slope gave constant  $k_5$  ( $k_5 = 4.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

For the variation of  $[\text{H}^+]$  at constant  $[\text{S}]$  the rate law (16) can be written as

$$k_{\text{obs}} = \frac{K_1 k_2 [\text{H}_2\text{O}]}{k + [\text{H}^+]} + k', \text{ where } k' = k_5 [\text{S}]$$

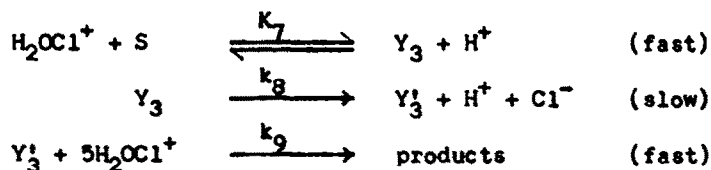
$$\text{or } (k_{\text{obs}} - k') = \frac{K_1 k_2 [\text{H}_2\text{O}]}{k + [\text{H}^+]} \quad (17)$$

$$\frac{1}{(k_{\text{obs}} - k')} = \frac{k}{K_1 k_2 [\text{H}_2\text{O}]} + \frac{[\text{H}^+]}{K_1 k_2 [\text{H}_2\text{O}]} \quad (18)$$

$$\frac{1}{(k_{\text{obs}} - k')} = \frac{1}{k_1} + \frac{[\text{H}^+]}{K_1 k_2 [\text{H}_2\text{O}]} \quad (19)$$

The plot of  $1/(k_{\text{obs}} - k')$  versus  $[\text{H}^+]$  was linear in accordance with rate law (19) (Fig.1) and the constant  $k_1$  was calculated ( $k_1 = 0.02 \text{ s}^{-1}$ ) from the intercept.

Scheme 1 depicts the decomposition of CAB into HOCl which in turn interact with the substrate to give the products. This was independently verified by studying the kinetics of oxidation of TSC by HOCl under identical conditions. The kinetics observed with HOCl were similar to CAB kinetics (Table 3) thus justifying the proposed mechanisms. The plots of  $k_{\text{obs}}$  versus  $[\text{S}]$  or  $1/k_{\text{obs}}$  versus  $1/[\text{S}]$  and  $1/k_{\text{obs}}$  versus  $[\text{H}^+]$  were also linear (Fig.1 and 2). The observed kinetics with HOCl can also be explained by



Scheme - 3

Applying steady state treatment, the rate law (20) has been obtained.

$$-\frac{d[\text{HOCl}]}{dt} = \frac{K_7 k_8 [\text{HOCl}][\text{S}]}{[\text{H}^+] + K_7 [\text{S}]} \quad (20)$$

or

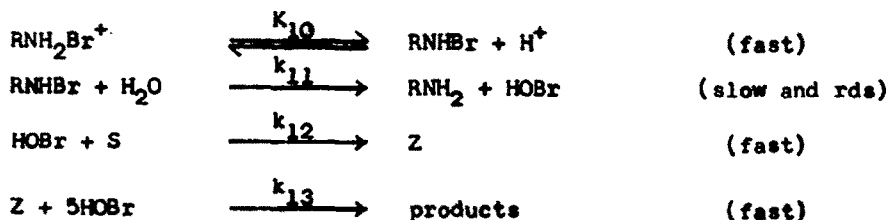
$$k_{\text{obs}} = \frac{K_7 k_8 [\text{S}]}{[\text{H}^+] + K_7 [\text{S}]} \quad (21)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+]}{K_7 k_8 [\text{S}]} + \frac{1}{k_8} \quad (22)$$

The constants  $K_7$  and  $k_8$  were calculated from the slope and intercept of the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{S}]$  ( $K_7 = 6.53$  and  $k_8 = 1.43 \times 10^{-3} \text{ s}^{-1}$ ).

ii) With bromamine-B and HOBr: In the case of bromamine-B oxidation, the rate was first order in  $[\text{BAB}]$ , zero order in  $[\text{S}]$  and inverse fractional order in  $[\text{H}^+]$ . The product BSA ( $\text{RNH}_2$ ) had no effect on the rate. These results can be accounted by Scheme 4 and rate law (23).



Scheme - 4

$$-\frac{d[\text{BAB}]}{dt} = \frac{K_{10}k_{11}[\text{BAB}][\text{H}_2\text{O}]}{[\text{H}^+] + (k_{11}/k_{-10})[\text{H}_2\text{O}]} \quad (23)$$

$$k_{\text{obs}} = \frac{K_{10}k_{11}[\text{H}_2\text{O}]}{[\text{H}^+] + (k_{11}/k_{-10})[\text{H}_2\text{O}]} \quad (24)$$

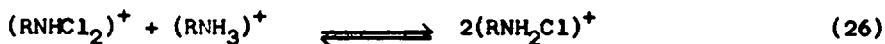
$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+]}{K_{10}k_{11}[\text{H}_2\text{O}]} + 1/k_{10} \quad (25)$$

The plot of  $1/k_{\text{obs}}$  versus  $[\text{H}^+]$  was linear in accord with rate law (25) (Fig.1) and the reciprocal of the intercept gave the constant  $k_{10}$  ( $k_{10} = 3.3 \times 10^{-3} \text{ s}^{-1}$ ).

The possibility of a part of BAB-TSC reaction going through a path identical to scheme-2 may be low with BAB as it is a better donator of positive halogen species than CAB.

To test the validity of scheme-4, HOBr-TSC reaction was investigated under identical conditions. The kinetics observed with the latter were identical to those of BAB-TSC reaction (Table-3) supporting the suggested mechanisms.

iii) With dichloramine-B: DCB-TSC reaction had a slight induction period probably signifying the catalysis by one of the products. This was confirmed by adding benzenesulphonamide (BSA)(Table 2). The rate was increased by the addition of a small quantity of BSA. But the further additions of the latter had no significant effect. The catalysis by BSA is probably due to the reaction first going through,



and then through a reaction path identical to scheme-1 and rate law (13).

$$K_{\text{obs}} = \frac{K_1k_2[\text{H}_2\text{O}]}{(k_2/k_{-1})[\text{H}_2\text{O}] + [\text{H}^+]}$$

$$\text{or } \frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+]}{K_1k_2[\text{H}_2\text{O}]} + \frac{1}{k_1} \quad (27)$$

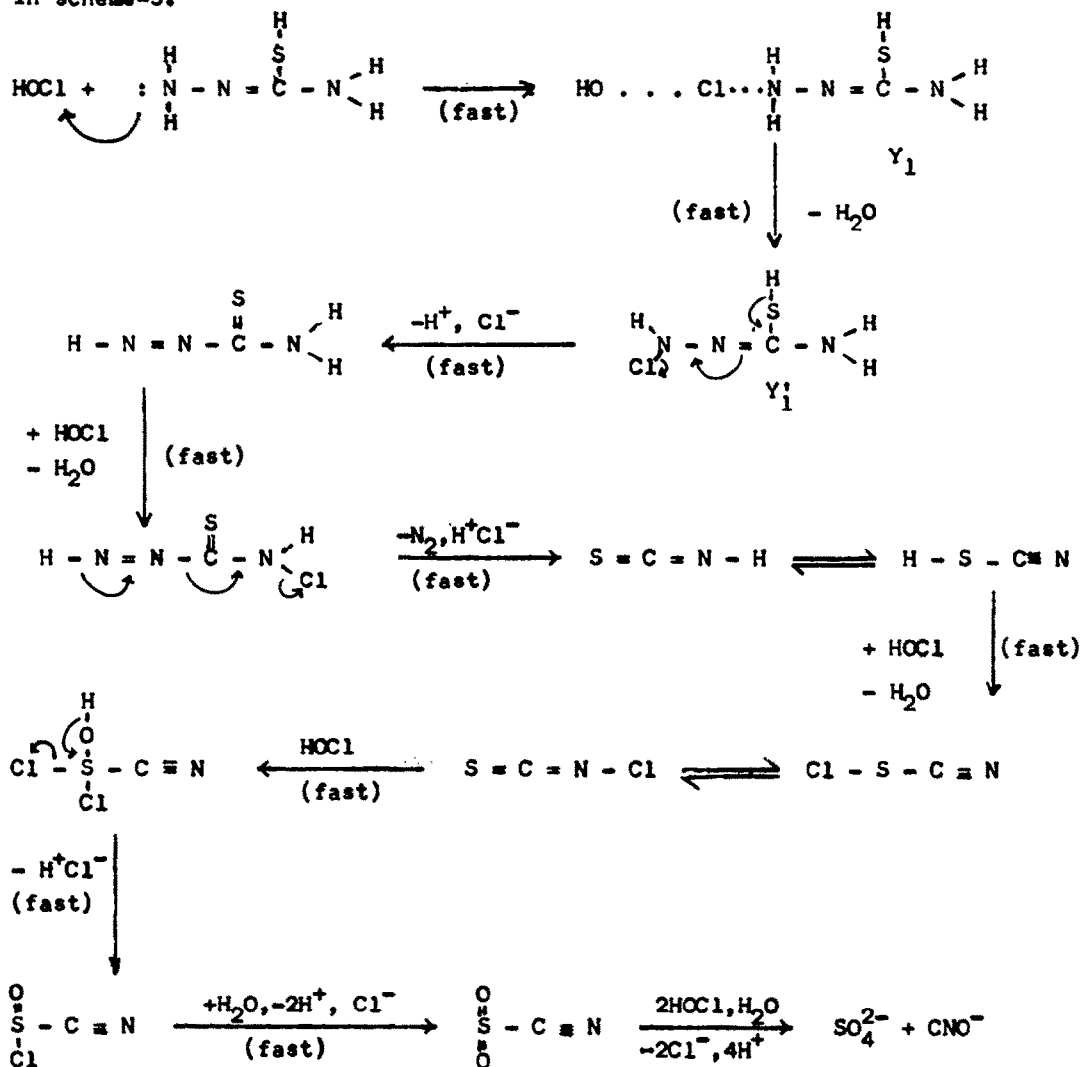
The plot of  $1/k_{\text{obs}}$  versus  $[\text{H}^+]$  was linear in conformity with rate law (27). The constant  $K_1$  was calculated from the intercept ( $k_1 = 1.5 \times 10^{-3} \text{ s}^{-1}$ ).

The proposed mechanisms are also supported by the moderate values of activation parameters. Almost the constancy of  $\Delta G^\ddagger$  for the oxidation by all the oxidants except DCB may indicate the operation of similar mechanism. The deviation with DCB is understandable as the reaction medium was different. The formation of more ordered activated complexes is evident from the negative  $\Delta S^\ddagger$  values.

Observed increase of rate with decrease in dielectric constant of the medium in the case of DCB is in accordance with Amis-Jaffe equation<sup>20</sup>.

The observed slight decrease of rate with increase in ionic strength of the medium is in conformity with Quinlan-Amis equation<sup>21</sup>.

The detailed mechanism of oxidation of thiosemicarbazide by HOCl is shown in scheme-5.



Scheme - 5

The intermediate  $Y_1$  formed by the interaction of HOCl and S undergoes disproportionation to give N-chloro derivative of the substrate which subsequently interacts with another five molecules of HOCl, in fast steps, as shown to give sulphate and cyanate as the final products.

Similarly HOBr interacts with the substrate to give N-bromo derivative which in turn undergoes disproportionation and further reactions with additional HOBr molecules to yield the products.

Table 1. Pseudo-first-order rate constant ( $k_{obs}$ ) for the oxidation of thiosemicarbazide (TSC) by chloramine-B (CAB), bromamine-B (BAB), dichloramine-B (DCB), Hypochlorite and Hypobromite at different [oxidant], [TSC] and  $[HClO_4]$  ( $\mu = 0.5 \text{ mol dm}^{-3}$ , Temp = 303 K).

$[X], \text{mol dm}^{-3}$				$10^4 k_{obs}, \text{s}^{-1}$				
$10^3[\text{oxidant}]$	$10^2[\text{TSC}]$	$10[\text{HClO}_4]$	$10^2[H^+]^a$	CAB	BAB	DCB	HOCl	HOBr
0.2	2.0	1.0	8.8	3.3	3.2	5.2	-	-
0.5	2.0	1.0	8.8	3.3	3.2	5.2	4.3	3.4
1.0	2.0	1.0	8.8	3.3	3.2	5.2	4.3	3.4
2.0	2.0	1.0	8.8	3.3	3.2	5.2	-	3.4
3.0	2.0	1.0	8.8	-	-	5.2	-	3.4
4.0	2.0	1.0	8.8	-	-	-	4.3	-
1.0	0.2	1.0	8.8	-	-	5.2	-	-
1.0	0.5	1.0	8.8	2.5	2.9	5.2	-	3.2
1.0	1.0	1.0	8.8	2.9	3.1	5.2	3.7	3.2
1.0	2.0	1.0	8.8	3.3	3.2	5.2	4.3	3.3
1.0	4.0	1.0	8.8	4.2	3.2	-	5.1	3.3
1.0	5.0	1.0	8.8	4.6	-	-	-	-
1.0	6.0	1.0	8.8	-	3.2	-	5.6	3.2
1.0	2.0	0.2	2.0	15.4	12.4	10.8	11.5	12.0
1.0	2.0	0.5	4.6	8.0	6.0	5.2	6.2	6.2
1.0	2.0	1.0	8.8	3.3	3.2	3.6	4.3	3.4
1.0	2.0	2.0	16.5	2.0	2.1	2.4	2.6	2.0

<sup>a</sup> Effective  $[H^+]$  at different  $[HClO_4]$ .

Table 2. Effects of ionic strength, solvent composition and the reduced product benzenesulphonamide on the rate of oxidation of TSC by CAB, BAB, DCB, HOCl and HOBr in perchloric acid medium. ( $\mu = 0.5 \text{ mol dm}^{-3}$  except during its variation; Temp = 303 K).

$\mu$ ( $\text{mol dm}^{-3}$ )	$10^4 k_{obs}, \text{s}^{-1}$				
	CAB <sup>a</sup>	BAB <sup>a</sup>	DCB <sup>b</sup>	HOCl <sup>a</sup>	HOBr <sup>a</sup>
0.12	4.3	3.7	7.5	5.1	3.7
0.2	3.7	3.3	6.8	4.7	3.6
0.5	3.3	3.2	5.2	4.3	3.4
1.0	3.0	2.9	-	4.1	3.3
x methanol					
0 (30)	3.3	3.2	2.3	4.3	3.4
5 (40)	3.3	3.2	3.8	4.3	3.4
10 (50)	3.2	3.3	5.2	4.4	3.4
20 (70)	3.2	3.3	7.2	4.3	3.3
40	3.1	3.4	-	4.3	3.4
$10^3[\text{BSA}]$					
(mol $\text{dm}^{-3}$ )					
0.0	3.3	3.2	5.2	-	-
0.1	3.3	3.2	7.3	-	-
0.5	3.3	3.2	7.6	-	-
1.0	3.3	3.2	7.7	-	-

<sup>a</sup>  $10^3[\text{oxidant}] = 50[\text{TSC}] = 10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$ .

<sup>b</sup>  $10^3[\text{DCB}] = 50[\text{TSC}] = 10[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$ , Medium 1:1 aqueous methanol (v/v).



Table 3. Kinetic and Thermodynamic Parameters for the oxidation of thiosemicarbazide by Chloramine-B(CAB), Bromamine-B(BAB), Dichloramine-B (DCB), HOCl and HOBr.

Orders Observed in	CAB	BAB	DCB	HOCl	HOBr
[oxidant]	1	1	1	1	1
[TSC]	0.28	0	0	0.25	0
[H <sup>+</sup> ]	- 0.95	- 0.8	- 0.84	- 0.7	- 0.8
<b>Parameter</b>					
log A	11.0	10.2	16.5	9.9	10.2
E <sub>a</sub> (kJ mol <sup>-1</sup> )	83.8	79.3	114.9	76.8	79.5
ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	81.3	76.7	112.4	74.3	76.9
ΔS <sup>‡</sup> (JK <sup>-1</sup> )	- 8.5	-12.0	17.0	- 13.4	- 11.8
ΔG <sup>‡</sup> (kJ mol <sup>-1</sup> )	83.8	80.3	111.5	78.4	80.5

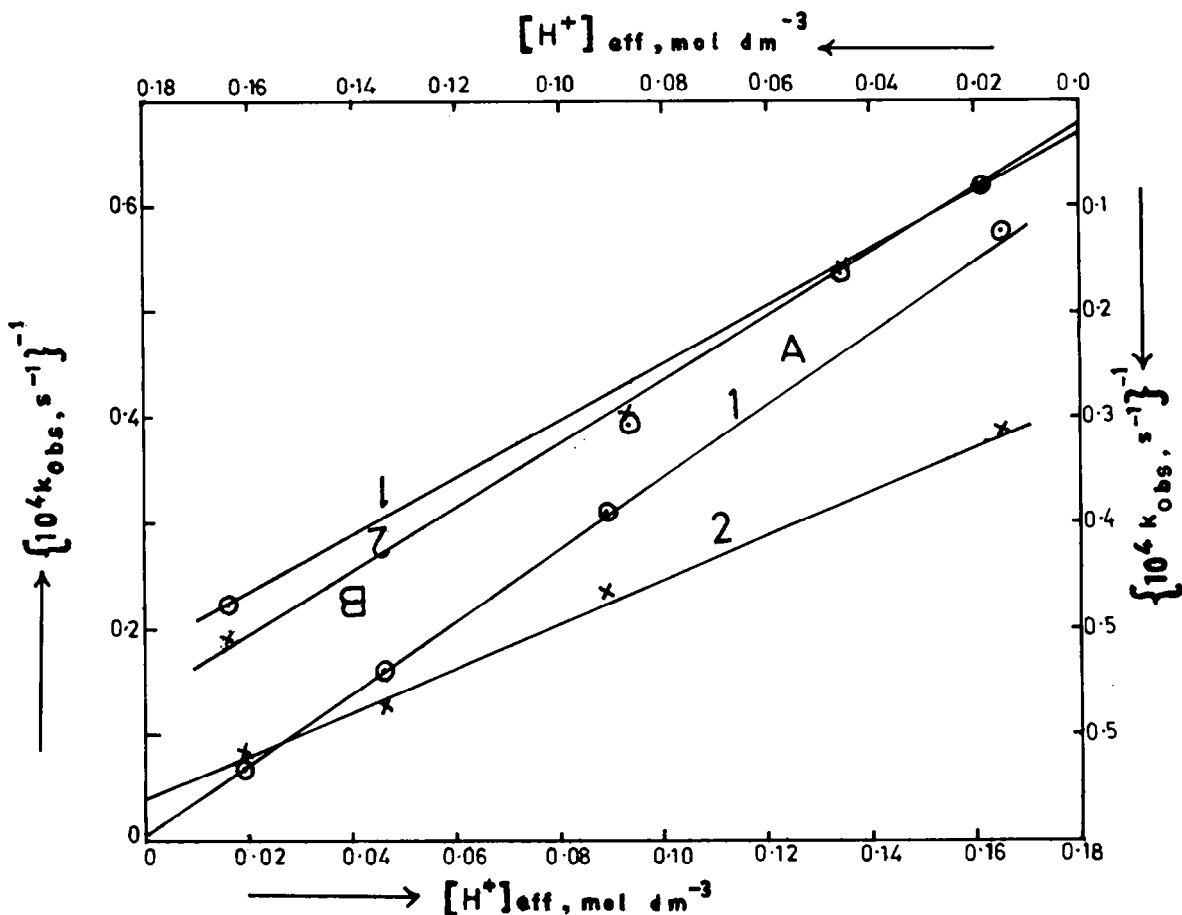


Figure 1: (A) (1) Plot of  $1/k_{obs} - k'$  versus  $[H^+]$ ; (2) Plot of  $1/k_{obs}$  versus  $[H^+]$ .  $10^3 [CAB\ or\ HOCl] = 50 [TSC] = 2\ \mu = 1.0\ mol\ dm^{-3}$ ; Temp = 303 K. (B) Plot of  $1/k_{obs}$  versus  $[H^+]_{eff}$ , BAB(1); HOBr(2).  $10^3 [BAB\ or\ HOBr] = 50 [TSC] = 2\ \mu = 1.0\ mol\ dm^{-3}$ ; Temp = 303 K.

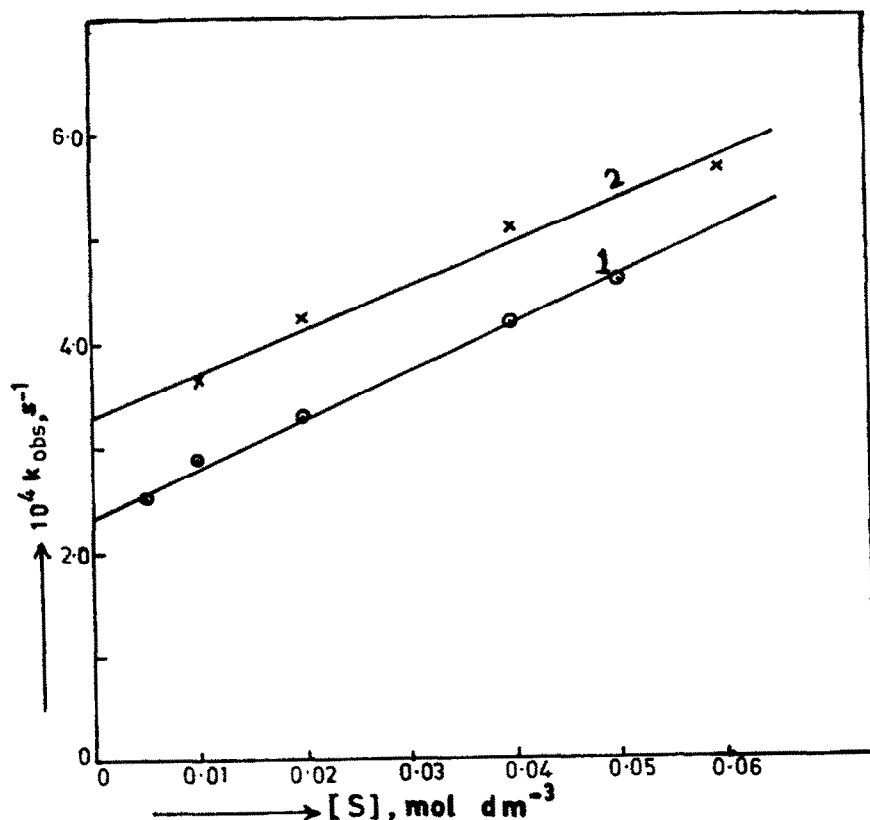


Figure 2 : Plot of  $k_{\text{obs}}$  versus  $[S]$ ; CAB(1) and HOCl(2).  
 $10^3[\text{CAB or HOCl}] = 1.0 \text{ mol dm}^{-3}$ ;  $10^2[\text{H}^+] = 8.8$   
 $\text{mol dm}^{-3}$ ;  $\mu = 0.5 \text{ mol dm}^{-3}$ ; Temp = 303 K.

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