Kinetics and Mechanism of Oxidation of Thiosemicarbazide in the Pure State and in its Metal Complex by Chloramine T, Bromamine T, and Dichloramine T in Acid Medium

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The kinetics and mechanism of oxidation of thiosemicarbazide (TSC) in the pure state and in its zinc metal complex by chloramine T (CAT) and bromamine T (BAT) in aqueous perchloric acid medium and by dichloramine T (DCT) in 1 : 1 (v/v) water–methanol medium have been investigated. The rate followed first-order kinetics in [oxidant] and fractional order in [TSC] in both the pure state and in the metal complex with all the oxidants. With chloramine T, the rate had an inverse first-order and inverse fractional order dependence in [H^+] for two ranges of [$HClO_4$], 0.01—0.05 and 0.05—0.3 mol dm^{-3}, respectively. The rate had inverse fractional and inverse first-order dependence in [H^+] with BAT and DCT respectively over the entire [$HClO_4$] range (0.01—0.2 mol dm^{-3}). Addition of the reduced product of the oxidants (toluene-*p*-sulphonamide) had no significant effect on the rate with all the oxidants. But the increase of ionic strength of the medium decreased the rate. Decrease of dielectric constant of the reaction medium by adding methanol increased the rate indicating positive ion–dipole interactions in the rate-limiting steps. The coefficients of the rate-limiting steps have been computed at different temperatures with all the oxidants and these constants were used to calculate the activation parameters from the Arrhenius plots. The oxidation process under the conditions employed has been shown to proceed by two paths, one involving the direct interaction of monochloramine T (RNHCl) or dichloramine T ($RNCl_2$) with TSC to give an *N*-chloro intermediate of the substrate which subsequently undergoes disproportionation and further reactions with the oxidant molecules in fast steps to give the final products, and the other involving the interaction of H_2OCl^+ or H_2OBr^+, produced from the disproportionation of oxidants, with the substrate to yield the products. The mechanisms proposed and the rate laws deduced are in conformity with the observed kinetics. The rate constants predicted by the derived rate laws as [TSC], [Complex], or [H^+] vary are in good agreement with the experimental rate constants thus justifying the rate laws and hence the suggested mechanistic schemes.

The chemistry of thiosemicarbazide (TSC) and its derivative thiosemicarbazones is of interest due to their biological activity and applications.[1–4] They are well known as metal-chelating agents and find application in the characterization of aldehydes, ketones, and polysaccharides. They are antitubercular active and found to be active against influenza, protozoa, smallpox, and certain kinds of tumour. They are also possible pesticides and fungicides.

Although *N*-halogeno-*N*-metallo and *NN*-dihalogenoaromatic sulphonamides have been extensively used for determining TSC in the pure state and in its metal complexes,[5] there are no reports on the mechanistic aspects of these reactions. The present investigation is a part of our kinetic and mechanistic studies with positive halogen in general and *N*-halogeno-*N*-metalloaromatic sulphonamides in particular.[6–9] We report herein the kinetics of oxidation of TSC in the pure state and in its metal complex by chloramine T and bromamine T in aqueous media and by dichloramine T in 50% (v/v) aqueous methanol.

Experimental

Materials and Methods.—Chloramine T ($CH_3C_6H_4SO_2$-NClNa, CAT) (E. Merck) was purified by a method reported elsewhere.[10] Dichloramine T ($CH_3C_6H_4SO_2NCl_2$, DCT) was prepared by the chlorination of CAT solution[11] and bromination of CAT yielded dibromamine T (DBT).[12] Partial debromination of DBT by dissolving it in 4 mol dm^{-3} sodium hydroxide gave bromamine T[13] ($CH_3C_6H_4SO_2NBrNa$, BAT). The purity of the oxidants was checked by recording their i.r. and n.m.r. spectra and by estimating, iodometrically, the amount of positive halogen present. Aqueous stock solutions (*ca.* 0.1 mol dm^{-3}) of CAT, BAT, and DCT in methanol were prepared, standardized, and stored in dark bottles.

Thiosemicarbazide (TSC) (E. Merck) was purified by recrystallization from the aqueous solution of the sample. The complex $Zn(TSC)_2SO_4$ was obtained by mixing concentrated aqueous solutions of TSC and the corresponding metal salts in 2:1 molar ratio and scratching the sides of the container.[3] The complex was recrystallized from aqueous solution and its composition was checked by elemental analysis. The complex was further characterized by recording its i.r. spectra. Aqueous stock solutions (0.1 mol dm^{-3}) of TSC and metal complex were prepared. The ionic strength of the reaction medium was kept at 0.3 mol dm^{-3} 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. Reactions with CAT and BAT were studied in aqueous media and DCT in 50% (v/v) aqueous methanol under pseudo-first-order conditions with [TSC] or [complex] always greater than [oxidant] by at least 5—20 times. The reactions were initiated by the rapid addition of the requisite amounts of oxidant solution, thermally pre-equilibrated at a desired temperature, to a mixture containing known amounts of TSC or complex, perchloric acid, sodium perchlorate solution, and water (and methanol with DCT to maintain 50% v/v solvent composition), pre-equilibrated at the same temperature. The progress of the reactions was monitored for at least two half-lives by iodometric determination of unchanged oxidant at regular intervals. Pseudo-first-order rate constants were computed by the method of least squares and were reproducible to within ±3%.

Stoicheiometry and Product Analysis.—TSC–CAT, TSC–BAT, and TSC–DCT stoicheiometries in the pure state and in its metal complex were determined by allowing the reactions to go to completion at 303 K at different $[H^+]$ (0.01—0.2 mol dm^{-3}) and [substrate]/[oxidant] ratios. The products, sulphate, cyanate, and cyanogen bromide, were detected by standard tests.[14–17] Further cyanogen bromide and sulphate were quantitatively estimated by iodometric[17] and gravimetric[18] methods, respectively. Toluene-*p*-sulphonamide (PTS), the reduced product of the oxidants, was detected by paper chromatography employing benzyl alcohol saturated with water as the solvent and 0.5% vanillin in 1% HCl solution in ether as the spray reagent (R_F 0.91). The observed stoicheiometries are represented by equations (1) and (2). Although the observed 1:6 stoicheiometry with CAT and DCT may also be represented by equation (3), corresponding to the formation of CO_2 and ammonia as products instead of CNO, the former are formed in negligible quantities.

$$H_2NNHCSNH_2 + 6RNClNa(\text{or } 3RNCl_2) + 5H_2O \longrightarrow 6RNH_2\ (\text{or } 3RNH_2) + SO_4^{2-} + CNO^- + N_2 + 6Cl^- + 6Na^+\ (\text{or } 6H^+) + 3H^+ \quad (1)$$

$$H_2NNHCSNH_2 + 6RNBrNa + 4H_2O \longrightarrow 6RNH_2 + SO_4^{2-} + CNBr + N_2 + 5Br^- + 6Na^+ + H^+ \quad (2)$$

$$R = CH_3C_6H_4SO_2$$

$$H_2NNHCSNH_2 + 6RNClNa\ (\text{or } 3RNCl_2) + 6H_2O \longrightarrow 6RNH_2\ (\text{or } 3RNH_2) + SO_4^{2-} + CO_2 + N_2 + NH_4^+ + 6Cl^- + 6Na^+\ (\text{or } 6H^+) + H^+ \quad (3)$$

Results

The kinetics of oxidation of TSC and its complex by CAT, BAT, DCT, and hypochlorite were investigated at several initial concentrations of the reactants and $HClO_4$ (0.01—0.2 mol dm^{-3}) (Tables 1—5). At constant [acid] with several-fold excess of the substrate (5—20 times), the plots of log $[\text{oxidant}]_0/[\text{oxidant}]$ *versus* time were linear for two half-lives for all the oxidants and pseudo-first-order rate constants were insensitive to change in $[\text{oxidant}]_0$ (Tables 1—3), establishing first-order kinetics in [oxidant] with all oxidants. At constant [oxidant] and [TSC] the rates decreased with increase in $[HClO_4]$ for all oxidants. But plots of log $k_{obs.}$ *versus* log $[H^+]_{eff.}$ were linear with varying slopes (Table 5). For the oxidation of TSC by CAT there were two ranges. The slopes were −1.0 and −0.7 in the $[HClO_4]$ ranges 0.01—0.05 and 0.05—0.3 mol dm^{-3}, respectively, indicating inverse first-order and inverse fractional order dependence in $[H^+]$ in the

Table 1. Pseudo-first-order rate constants ($k_{obs.}$) for the oxidation of thiosemicarbazide (TSC) by chloramine T (CAT) at different [TSC], [CAT], and $[HClO_4]$ (μ 0.3 mol dm^{-3}, *T* 308 K)

				$10^4k_{obs.}/s^{-1}$ at $[HClO_4]$/mol dm^{-3}		
$10^2[HClO_4]^a$/mol dm^{-3}	$10^2[H^+]_{eff.}$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$	$10^3[CAT]^b$/mol dm^{-3}	0.02	0.05	0.10
1.0	0.96	48.6	0.2	23.6	9.2	5.6
1.5	1.45	34.8	0.5	23.7	9.0	5.5
2.0	1.89	23.7	1.0	23.7	8.9	5.5
3.0	2.85	14.6	2.0	23.7	9.2	5.5
4.0	3.69	10.8				
			$10^2[TCS]^c$/mol dm^{-3}			
5.0	4.6	8.9	0.75	19.7		4.9
10.0	8.8	5.5	1.0	23.7	8.9	5.5
15.0	12.7	4.1	2.0	34.1	11.7	7.0
20.0	16.5	3.3	4.0	48.6	15.7	8.6
30.0		2.5	5.0	57.2	18.6	9.6

[a] $10^3[CAT] = 10^2[TSC] = 1.0$ mol dm^{-3}. [b] $10^2[TSC]$ 1.0 mol dm^{-3}. [c] $10^3[CAT]$ 1.0 mol dm^{-3}.

Table 2. Pseudo-first-order rate constants ($k_{obs.}$) for the oxidation of TSC by BAT (aqueous medium) at 308 K and DCT (1:1 water–methanol) at 303 K (μ 0.3 mol dm^{-3})

		$10^4k_{obs.}/s^{-1}$			$10^4k_{obs.}/s^{-1}$	
$10^2[HClO_4]^a$/mol dm^{-3}	$10^2[H^+]_{eff.}$/mol dm^{-3}	BAT	DCT	$10^3[\text{oxidant}]^b$/mol dm^{-3}	BAT	DCT
1.0	0.96		33.8	0.2	9.9	8.1
2.0	1.89	18.6	18.3	0.5	9.7	8.0
4.0	3.69	11.5		1.0	9.9	8.1
5.0	4.6	9.9	8.1	2.0	10.0	8.2
7.5	6.7	7.2				
				$10^2[TSC]^c$/mol dm^{-3}		
10.0	8.8	6.0	4.1	0.75	8.3	7.5
20.0	16.5	4.2	2.24	1.0	9.9	8.1
				2.0	13.8	9.6
				5.0	22.5	12.3

[a] $10^3[\text{oxidant}] = 10^2[TSC] = 1.0$ mol dm^{-3}. [b] $10^2[TSC] = 20[HClO_4] = 1.0$ mol dm^{-3}. [c] $10^3[\text{oxidant}] = 20[HClO_4] = 1.0$ mol dm^{-3}.

Table 3. Pseudo-first-order rate constants ($k_{obs.}$) for the oxidation of $Zn(TSC)_2SO_4$ complex by CAT and BAT (μ 0.3 mol dm^{-3}, T 303 K) at different [reactant] and [$HClO_4$]

		$10^4k^a_{obs.}/s^{-1}$	10^4[oxidant]^c/mol dm^{-3}		$10^4k_{obs.}/s^{-1}$	
$10^2[HClO_4]$/mol dm^{-3}	$10^2[H^+]_{eff.}$/mol dm^{-3}	CAT	CAT	BAT	CAT	BAT
3.0	2.85	11.9	2.0	2.0	7.6	5.5
5.0	4.6	7.7	5.0	5.0	7.7	5.6
10.0	8.8	4.2	10.0	10.0	7.6	5.5
20.0	16.5	2.83	20.0	20.0	7.7	5.5
		BAT^b	10^3[complex]^c/mol dm^{-3}			
2.0	1.89	11.4	2.5	5.0	5.2	3.65
3.0	2.85	7.9	5.0	10.0	7.7	5.5
5.0	4.6	5.5	10.0	15.0	12.7	7.1
10.0	8.8	3.15	15.0	20.0	16.9	8.6
20.0	16.5	1.86		40.0		13.3

^{a} 10^4[CAT] = 10^3[complex] = 5.0 mol dm^{-3}. ^{b} 10^3[BAT] = 10^2[complex] = 1.0 mol dm^{-3}. ^{c} $10^2[HClO_4]$ = 5.0 mol dm^{-3}.

Table 4. Pseudo-first-order rate constants ($k_{obs.}$) for the oxidation of TSC by hypochlorite at 303 K (μ 0.5 mol dm^{-3})

$10^3[OCl^-]^a$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$	$10^2[HClO_4]^c$/mol dm^{-3}	$10^2[H]_{eff.}$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
0.5	4.3	2.0	1.9	11.5
1.0	4.3	5.0	4.6	6.2
2.0	4.3	10.0	8.8	4.3
4.0	4.3	20.0	16.5	2.6
10^2[TSC]^b		10.0^d	8.8	5.1
1.0	3.7	10.0^e	8.8	4.7
2.0	4.3			
4.0	5.1	10.0^f	8.8	4.1
6.0	5.6			

^{a} 50[TSC] = 1.0 mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3}. ^{b} $10^3[OCl^-]$ = $10[HClO_4]$ = 1.0 mol dm^{-3}. ^{c} $10^3[OCl^-]$ = 50[TSC] = 1.0 mol dm^{-3}. μ (mol dm^{-3}): ^{d} 0.12. ^{e} 0.2. ^{f} 1.0.

Table 5. Kinetic and thermodynamic parameters for the oxidation of TSC in the pure state and in its metal complex by CAT, BAT, and DCT and the effect of varying ionic strength and solvent composition of the medium on the rate of oxidation

Orders observed in	CAT at [H^+]/mol dm^{-3}					$Zn(TSC)_2SO_4$	
	0.02	0.05	0.1	BAT	DCT	CAT	BAT
[TSC]	0.6	0.5	0.4	0.5	0.3	0.6	0.6
[oxidant]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[H^+]	−1.0	−0.7	−0.7	−0.6	−1.0	−0.8	−0.8

Activation parameters	log A	E_a/kJ mol^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$/kJ mol^{-1}
CAT	7.88	57.9	55.4	−94.2	83.9
BAT	18.5	124.7	122.1	109.2	89.0
DCT	9.78	74.7	71.8	−57.8	89.3

	$10^4k_{obs.}/s^{-1}$				$10^4k_{obs.}/s^{-1}$		
μ/mol dm^{-3}	CAT^a	BAT^b	DCT^b	% Methanol^c	CAT^a	BAT^b	DCT^b
0.2	24.8	10.2		10 (50)	24.6	11.0	8.1
0.3	23.7	9.9	8.1	20 (60)	25.8	11.5	9.7
0.5	21.9	8.8	6.1	30 (70)	27.9	11.7	11.5
0.75			4.8				

^{a} 10^3[CAT] = 10^2[TSC] = $50[HClO_4]$ = 1.0 mol dm^{-3}. ^{b} 10^3[oxidant] = 10^2[TSC] = $20[HClO_4]$ = 1.0 mol dm^{-3}. ^{c} Values in parentheses are for DCT.

respective ranges. There was only one range for the oxidation of TSC by BAT and for complex oxidations by both CAT and BAT, with inverse fractional order in [H^+]. The rate had nearly inverse first-order dependence in [H^+] with DCT (Table 2). At constant [$HClO_4$] and [oxidant]$_0$, the rates increased with increase in [TSC] or [complex] in all cases. With CAT, [TSC] was varied at three different [$HClO_4$] (0.02, 0.05, and 0.1 mol dm^{-3}). Plots of log $k_{obs.}$ *versus* log [TSC] were linear with varying fractional slopes for all oxidants both in the pure state and in metal complex (Table 5), establishing fractional order dependence of rate on [TSC] in all cases. But the fractional order in [TSC] with CAT decreased with increase in [$HClO_4$] of the reaction medium while zinc complexation of the substrate increased the dependence of rate on its concentration. With hypochlorite the rate of oxidation followed first-order kinetics in [oxidant], fractional order in [TSC], and inverse fractional order in $[H^+]$.

An increase of the ionic strength of the reaction medium slightly decreased the rate with CAT and BAT and the effect was considerable with DCT. But the addition of the product PTS had no significant effect for all oxidants (Table 5). A decrease of dielectric constant of the medium by changing the solvent composition with methanol slightly increased the rate with all oxidants. Plots of log $k_{obs.}$ *versus* $1/D$ were linear with positive slopes.

The rates were measured at different temperatures as a function of [substrate] and the rate coefficients for the rate-limiting steps were calculated at different temperatures. The latter constants were used to calculate the activation parameters from the Arrhenius plots with all oxidants (Table 5).

Discussion

Chloramine T[6,19,20] and bromamine T[21] (RNXNa, where X = Cl or Br) are moderately strong electrolytes in aqueous solution and they furnish different reactive species, depending upon the pH of the reaction medium. Equilibria (4)—(10) exist in aqueous solutions of CAT, BAT, and DCT (RNX_2).

$$RNXNa \rightleftharpoons RNX^- + Na^+ \qquad (4)$$

$$RNX^- + H^+ \rightleftharpoons RNHX \qquad (5)$$

(K_a of RNHCl 2.82×10^{-5} at 25 °C)[19]

$$2RNHX \rightleftharpoons RNX_2 + RNH_2 \qquad (6)$$

(K_d of RNHCl 0.058 at 25 °C)[19]

$$RNX_2 + H_2O \rightleftharpoons RNHX + HOX \qquad (7)$$

(K_h of $RNCl_2$ 8.0×10^{-7} at 25 °C)[19]

$$RNHX + H_2O \rightleftharpoons RNH_2 + HOX \qquad (8)$$

(K_h of RNHCl 4.88×10^{-8} at 25 °C)[19]

$$RNHX + H^+ \rightleftharpoons RNH_2X^+ \qquad (9)$$

$$HOX + H^+ \rightleftharpoons H_2OX^+ \qquad (10)$$

Therefore the possible reactive species in acid solutions of CAT, BAT, and DCT are RNHX, RNX_2, and HOX at low $[H^+]$ and RNH_2X^+, RNX_2H^+, and H_2OX^+ at high $[H^+]$.

The protonation equilibrium (11) exists in acid solutions of

$$S + H^+ \rightleftharpoons SH^+ \qquad (11)$$

thiosemicarbazide (S). Under strong acidic conditions most of the substrate will be present as SH^+. It is also evident from the decrease of rate as $[HClO_4]$ increased, with all oxidants, that the protonated species is more difficult to oxidize than the unprotonated species.

Mechanism of Oxidations.—(a) *With chloramine* T. In the case of CAT, the order in $[H^+]$ was dependent on the concentrations. It was inverse first-order at low $[H^+]$ (up to 0.05 mol dm^{-3}) and fractional order at high $[H^+]$ (> 0.04 mol dm^{-3}).

(i) At low $[HClO_4]$ (< 0.05 mol dm^{-3}). The first-order kinetics in [CAT], fractional order in [S], and inverse first-order in $[H^+]$ and the observed lack of influence of the product (PTS) may be accounted for by Scheme 1 for at weakly acid solution; there will be alternative unprotonated sites for attack and hence substrate protonation equilibrium can be ignored. Applying the steady-state approximation to the intermediate Y_1, we have equation (12a) where $[RNHCl] = [RNHCl]_0 - [Y_1]$ and $[S]_0 \approx [S]$. If we then make the following assumptions that k_3 is negligible compared with other terms in the denominator and $[RNHCl]_0 = K_1[RNH_2Cl^+]_0/[H^+] = K_1[CAT]_0/[H^+]$, then equation (12a) becomes (12b). The rate of the reaction is then given by equation (13a). The rate law (13a) can also be written as (13b). If we now make the further assumption that $-1/[CAT]_0\, d[CAT]/dt \approx d\ln[CAT]/dt \approx k_{obs.}$, then the rate law (14) explains the rate data.

$$RNH_2Cl^+ \overset{K_1}{\rightleftharpoons} RNHCl + H^+ \qquad \text{(fast)}$$

$$RNHCl + NH_2NHCSNH_2 \overset{K_2}{\rightleftharpoons} Y_1\,(RNHCl \ldots NH_2NHCSNH_2) \qquad \text{(fast)}$$

$$Y_1 \xrightarrow{k_3} Y_2\,(NHNCSNH_2) + RNH_2 + H^+ + Cl^- \qquad \text{(slow and r.d.s.)}$$

$$Y_2 + 5RNHCl \xrightarrow{k_4} \text{products} \qquad \text{(fast)}$$

Scheme 1.

$$[Y_1] = \frac{k_2[RNHCl]_0[S]}{k_{-2} + k_3 + k_2[S]} \qquad (12a)$$

$$[Y_1] = \frac{k_2[RNHCl]_0[S]}{k_{-2} + k_2[S]} = \frac{K_2[RNHCl]_0[S]}{1 + K_2[S]}$$

$$[Y_1] = \frac{K_1K_2[CAT]_0[S]}{[H^+]\{1 + K_2[S]\}} \qquad (12b)$$

$$-\frac{d[CAT]}{dt} = \frac{K_1K_2k_3[CAT]_0[S]}{[H^+]\{1 + K_2[S]\}} \qquad (13a)$$

$$-\frac{1}{[CAT]_0}\frac{d[CAT]}{dt} = \frac{K_1K_2k_3[S]}{[H^+]\{1 + K_2[S]\}} \qquad (13b)$$

$$k_{obs} = \frac{K_1K_2k_3[S]}{[H^+]\{1 + K_2[S]\}}$$

$$\frac{1}{k_{obs.}} = \left\{\frac{1}{K_1K_2k_3[S]} + \frac{1}{K_1k_3}\right\}[H^+] \qquad (14)$$

The rate law (14) predicts linear plots between $k_{obs.}$ and $1/[H^+]$ or $1/k_{obs.}$ and $[H^+]$ and $1/k_{obs.}$ and $1/[S]$.

Plots of $k_{obs.}$ *versus* $1/[H^+]$ or $1/k_{obs.}$ *versus* $[H^+]$ were linear with no intercept and $1/k_{obs.}$ *versus* $1/[S]$ were linear with a finite intercept on the ordinate (Figure 1) confirming the rate laws. The ratio of intercept and slope of the latter plot gave K_2. The product $K_1K_2k_3$ and K_2 were used to predict the rate constants for the variation of $[H^+]$. The predicted rate constants compared with the experimental values are as follows:

$10^2[H^+]$/mol dm^{-3}		0.96	1.45	1.89	2.85	3.69	4.57
10^4k/s^{-1}	Calc.	48.0	31.8	24.4	16.2	12.5	10.1
	Obs.	48.6	34.8	23.7	14.6	10.8	8.9

A very good agreement between the two sets of values confirms the validity of the rate law and hence the proposed mechanism to explain the results.

(ii) At high $[HClO_4]$ (> 0.04 mol dm^{-3}). Under these conditions the rate of oxidation was first order in [CAT], smaller fractional order in [TSC], and inverse fractional order in $[H^+]$. Contrary to expectations, the kinetic order in [TSC] decreased from 0.6 to 0.4 as $[HClO_4]$ increased from 0.02 to 0.1 mol dm^{-3} (Table 5). At high $[HClO_4]$ most of the substrate

Table 6. Comparison of predicted[a] and experimental rate constants for the oxidation of TSC and its metal complex by chloramine T and bromamine T

$10^2[H^+]$/mol dm^{-3}	$10^4k_{calc}/s^{-1}$ TSC	$10^4k_{calc}/s^{-1}$ Complex	$10^4k_{obs.}/s^{-1}$ TSC	$10^4k_{obs.}/s^{-1}$ Complex	10^2[TSC]/mol dm^{-3}	$10^4k_{calc}/s^{-1}$ TSC	$10^4k_{calc}/s^{-1}$ Complex	$10^4k_{obs}/s^{-1}$ TSC	$10^4k_{obs}/s^{-1}$ Complex
	Chloramine T								
2.85		10.9		11.9	0.25		4.7		5.2
3.7	9.9		10.8		0.5		8.0		7.7
4.6	8.7	8.2	8.9	7.7	1.0	8.5	12.4	8.9	12.7
8.8	5.6	5.1	5.5	4.2	1.5		15.1		16.9
12.7	4.2		4.1		2.0	12.3		11.7	
16.5	3.4	3.1	3.3	2.8	4.0	15.9		15.7	
					5.0	16.8		18.6	
	Bromamine T								
1.89	15.9	9.9	18.6	11.4	0.5		4.1		3.7
2.85		8.0		7.9	0.75	8.1		8.3	
3.7	11.4		11.5		1.0	10.0	6.6	9.9	5.5
4.6	10.0	6.0	9.9	5.5	2.0	15.8	9.6	13.8	8.6
6.7	7.7		7.2		4.0	22.1	12.3	19.0	13.3
8.8	6.3	3.7	6.0	3.2	5.0	24.1		22.5	
16.5	3.8	2.2	4.2	1.9					

[a] See text and equation (17).

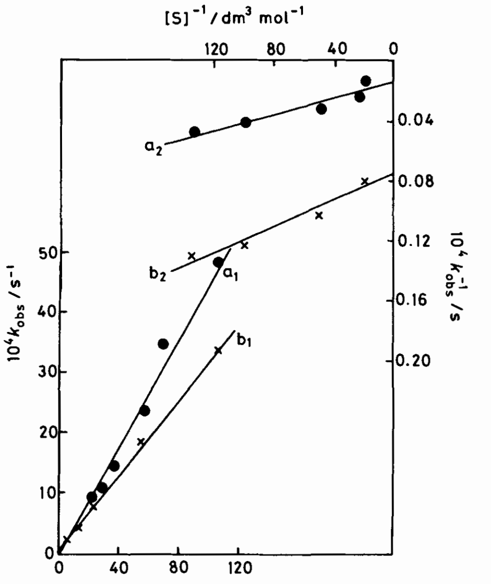


Figure 1. a_1, b_1, Plots of $k_{obs.}$ *versus* $1/[H^+]_{eff.}$; a_2, b_2, plots of $1/k_{obs.}$ *versus* $1/[S]$; a_1, a_2, 10^3[CAT] 1.0 mol dm^{-3}, μ 0.3 mol dm^{-3}, *T* 308 K; a_1, 10^2[TSC] 1.0 mol dm^{-3}; a_2, $10^2[H^+]$ 1.89 mol dm^{-3}; b_1, b_2, 10^3[DCT] 1.0 mol dm^{-3}, μ 0.3 mol dm^{-3}, *T* 303 K; b_1, 10^2[TSC] 1.0 mol dm^{-3}, b_2, $10^2[H^+]$ 4.6 mol dm^{-3}

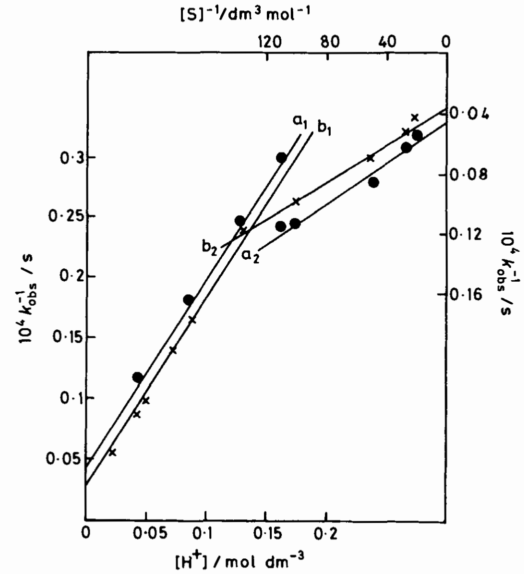


Figure 2. a_1, b_1, Plots of $1/k_{obs.}$ *versus* $[H^+]_{eff.}$; a_2, b_2, plots of $1/k_{obs.}$ *versus* $1/[S]$; a_1, a_2, 10^3[CAT] 1.0 mol dm^{-3}, μ 0.3 mol dm^{-3}, *T* 308 K; a_1, 10^2[TSC] 1.0 mol dm^{-3}; a_2, $10^2[H^+]$ 4.6 mol dm^{-3}; b_1, b_2, 10^3[BAT] 1.0 mol dm^{-3}, μ 0.3 mol dm^{-3}, *T* 308 K; b_1, 10^2[TSC] 1.0 mol dm^{-3}; b_2, $10^2[H^+]$ 4.6 mol dm^{-3}

would be present in the protonated form and if RNHCl continued to be the reactive species even under these conditions one would expect much greater dependence of rate on [TSC] as the protonated species (SH^+) is more difficult to oxidize than the unprotonated form (S). The decrease in dependence of rate on [TSC] as $[H^+]$ increased indicates that the reactive oxidizing species under highly acid conditions is different. H_2OCl^+ or RNH_2Cl^+ are likely to be the most probable and favourable reactive species under these conditions. As they are better oxidizing agents than HOCl or RNHCl, the decrease in dependence of rate on [TSC] in expected. This assumption was independently verified by studying the kinetics of oxidation of TSC by hypochlorite under identical conditions (Table 4). The kinetics were similar to those of CAT at high $[H^+]$, thus justifying the assumption. Hence the observed kinetics with CAT under highly acid conditions can be explained by Scheme 2. Applying the steady-state approximation to the intermediate

$$SH^+ \underset{}{\overset{K_5}{\rightleftharpoons}} S + H^+ \qquad \text{(fast)}$$

$$S + H_2OCl^+ \overset{K_6}{\rightleftharpoons} Y_1' \; (H_2OCl^+ \ldots NH_2NHCSNH_2) \qquad \text{(fast)}$$

$$Y_1' \xrightarrow{k_7} Y_2 + H_3O^+ + H^+ + Cl^- \qquad \text{(slow and r.d.s.)}$$

$$Y_2 + 5H_2OCl^+ \xrightarrow{k_8} \text{products} \qquad \text{(fast)}$$

Scheme 2.

Y_1' and with assumptions as above, rate laws (15)—(17) have been deduced.

$$-\frac{d[CAT]}{dt} = \frac{K_5K_6k_7[CAT]_0[SH^+]}{[H^+] + K_5K_6[SH^+]} \qquad (15)$$

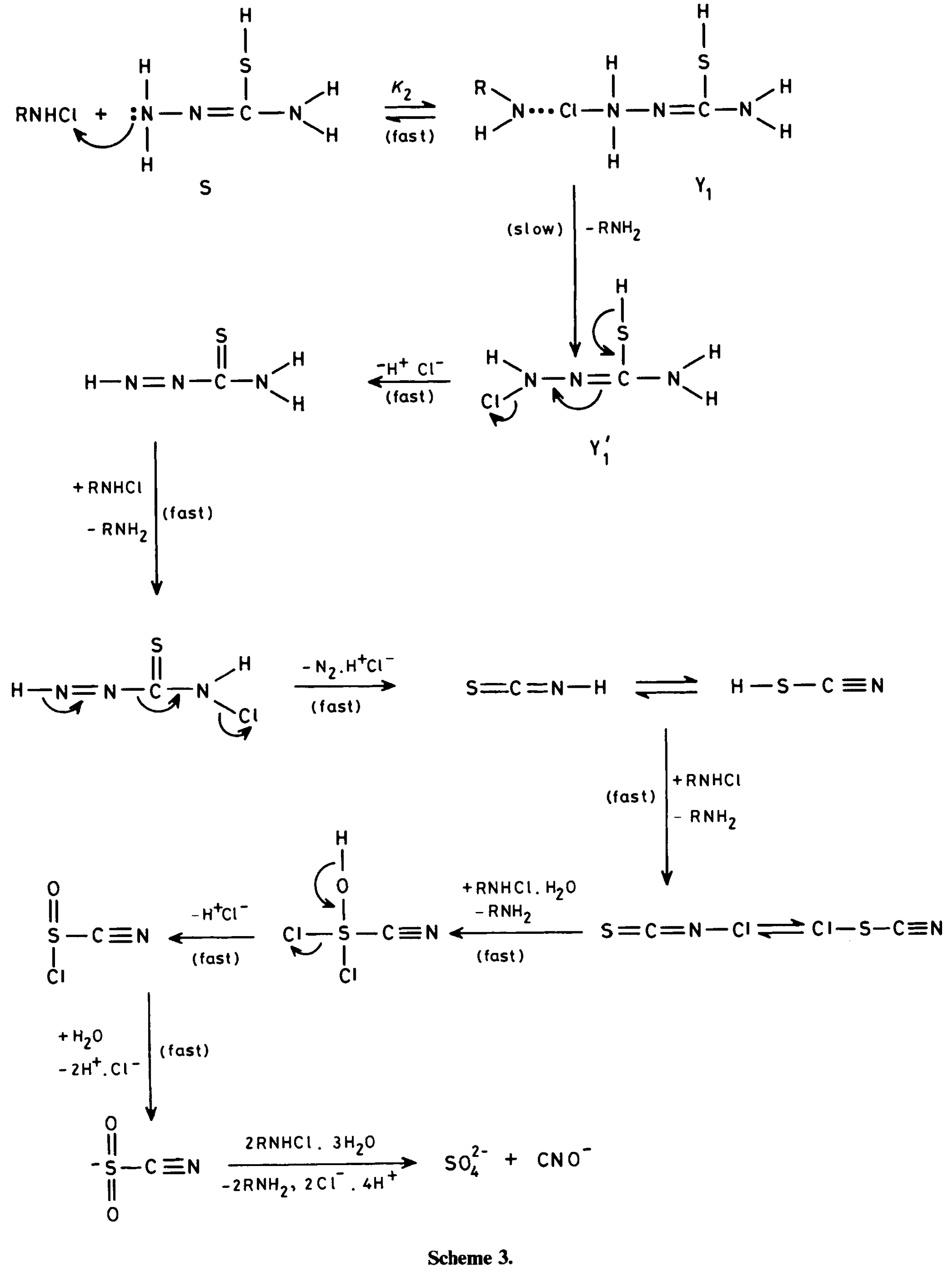
where $[S] = \frac{K_5[SH^+]}{[H^+]}$

$$k_{obs.} = \frac{K_5K_6k_7[SH^+]}{[H^+] + K_5K_6[SH^+]} \qquad (16)$$

$$\frac{1}{k_{obs.}} = \frac{[H^+]}{K_5K_6k_7[SH^+]} + \frac{1}{k_7} \qquad (17)$$

Rate law (17) predicts linearity between $1/k_{obs.}$ and $[H^+]$ or $1/[S]$. Plots of $1/k_{obs.}$ *versus* $1/[S]$, and $1/k_{obs.}$ *versus* $[H^+]$ (Figure 2), were linear with finite intercepts justifying rate law (17). The constants k_7 and K_5K_6 computed from a plot of $1/k_{obs.}$ *versus* $1/[S]$ were used to predict the rate constants by rate law (17) as $[H^+]$ was varied and *vice versa*. The predicted values compared with experiment are shown in Table 6. A very good agreement between the predicted and experimental rate constants tests the validity of the derived rate law and hence the proposed mechanism to account for the observed kinetics. It is important to note that the oxidation of TSC by CAT takes place through Schemes 1 and 2. Scheme 1 is predominant at low $[H^+]$ and Scheme 2 at high $[H^+]$. Both Schemes are satisfactory around 0.05 mol dm^{-3} H^+. Scheme 1 stretches up to 0.05 mol dm^{-3} H^+ and Scheme 2 down to 0.04 mol dm^{-3} H^+, *i.e.* both the kinetic analyses fit data around 0.05 mol dm^{-3} $[H^+]$.

Identical kinetics to those observed in the oxidation of TSC are found in Zn–TSC complex (Table 5) and can be explained by same Scheme 2 and rate law (17) (Table 6).



Scheme 3.

The substrate concentrations were varied at different temperatures and the coefficient of the rate-limiting step (k_7) was calculated as a function of temperature. These constants were used to compute the activation parameters from the Arrhenius plots of log k_7 *versus* $1/T$ and log (k_7/T) *versus* $1/T$ (Table 5).

(b) *With bromamine T*. In the case of oxidations with BAT, the same first-order kinetics in [BAT], fractional order in [S], and inverse fractional order in $[H^+]$ were observed over the entire range of $[HClO_4]$ (0.02—0.2 mol dm^{-3}) both in the pure state and in the metal complex. The product PTS had no effect on the rate. These results can be explained by a Scheme identical to Scheme 2 (replacing H_2OCl^+ by H_2OBr^+) and rate law (17). The constants computed from double reciprocal plots of $k_{obs.}$ and [S] (Figure 2) were used to predict the rate constants by rate law (17) as $[H^+]$ varied and *vice versa* (Table 6). As can be seen there is a good agreement between the predicted and experimental values, suggesting that the BAT–TSC reaction goes through a Michaelis–Menten-type mechanism over the entire range of $[HClO_4]$ rather than *via* a two-pathway mechanism.

The activation parameters were computed by calculating k_7 at different temperatures by the same procedure as for CAT (Table 5).

(c) *With dichloramine T*. In the case of oxidation with DCT, the rate was also first order in [DCT], but of smaller fractional order in [S] and nearly inverse first-order in $[H^+]$. The reduced product PTS had no effect on the rate. These results can be explained by a Scheme similar to Scheme 1 and rate law (14). As predicted by the latter, plots of $k_{obs.}$ *versus* $1/[H^+]$ or $1/k_{obs.}$ *versus* $[H^+]$ and $1/k_{obs.}$ *versus* $1/[S]$ were linear providing support for the suggested mechanism. The constants K_2 and $K_1K_2k_3$ were computed from the double reciprocal plot of $k_{obs.}$ *versus* [S] and these constants were used to predict the rate constants from rate law (11) for the variation of $[H^+]$:

$10^2[H^+]$/mol dm^{-3}	0.96	1.89	4.6	8.8	16.5
$10^4k_{calc.}$/s^{-1}	40.3	20.5	8.4	4.4	2.3
$10^4k_{obs.}$/s^{-1}	33.8	18.3	8.1	4.1	2.3

Reasonable agreement between the predicted and experimental rate constants confirms the validity of rate law (11) and hence the proposed mechanism.

Comparison of kinetic data reveals that BAT is a better oxidizing agent than CAT and DCT. The oxidizing ability of BAT is *ca.* 1.1 times that of CAT under identical reaction conditions. In other words BAT donates Br^+ species much more readily than CAT and DCT do Cl^+ species. Aqueous methanol medium seems to be the better medium for the purpose under investigation.

Zinc complexation of the substrate decrease the reactivity. The complexation of TSC not only affects the rate of oxidation but also the kinetic parameters. The rate of oxidation under these conditions is more dependent on [substrate] and $[H^+]$ (Table 5).

The detailed mechanism of oxidation of thiosemicarbazide by RNHCl is shown in Scheme 3.

The intermediate Y_1 formed by the interaction of RNHCl and S undergoes disproportionation in a slow step to give the *N*-chloro derivative of the substrate which subsequently interacts with another five molecules of RNHCl in fast steps to give sulphate and cyanate as the final products.

Similarly H_2OCl^+, H_2OBr^+, or $RNCl_2$ interact with the unprotonated form of the substrate to give the *N*-chloro derivative (Y_2, Y'_2 *etc.*) which in turn undergoes disproportionation and further reactions with additional oxidant molecules to yield products. Solvent effects on the rates of ion–ion, ion–dipolar molecule, and dipolar molecule–dipolar molecule reactions have been described.[22–25] The rate constant for an ion–dipolar molecule reaction in a medium of dielectric constant D is given by the modified Amis–Jaffé equation (18)[24]

$$\log k_D = \log k_\infty + \frac{ze\,\mu_0}{2.303\,kTr^2D} \qquad (18)$$

where k_∞ is the rate constant in a medium of infinite dielectric constant, ze is the charge on the ion, μ_0 the permanent moment on the dipole, r the radius of the ion, and T the absolute temperature.

Equation (18) predicts a linear relationship between log k_D and $1/D$ with a positive slope if ze is positive and negative slope if ze is negative. The increase of rate with a decrease in dielectric constant of the reaction medium observed in the present investigation is in conformity with equation (18) and hence with the proposed reactions schemes which involve mostly positive ion–dipolar molecule interactions. Further the plots of log $k_{obs.}$ *versus* $1/D$ were linear with positive slopes in all cases.

The observed slight decrease of rate with increase in ionic strength of the medium is in accordance with the Quinlan–Amis equation for ion–dipolar molecule reaction.[24,26]

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References

1 M. A. Ali and S. E. Livingstone, *Co-ord. Chem. Rev.*, 1974, **13**, 101.

2 M. J. M. Campbell, *Co-ord. Chem. Rev.*, 1975, **15**, 279 and references therein.

3 D. S. Mahadevappa and A. S. A. Murthy, *Aust. J. Chem.*, 1972, **25**, 1565.

4 D. S. Mahadevappa, B. T. Gowda, and A. S. A. Murthy, *Indian J. Chem.*, 1976, **14A**, 985.

5 B. T. Gowda and D. S. Mahadevappa, *Microchem. J.*, 1983, **28**, 374 and references therein.

6 B. T. Gowda and D. S. Mahadevappa, *J. Chem. Soc., Perkin Trans. 2*, 1983, 323.

7 B. T. Gowda and R. V. Rao, *Indian J. Chem.*, 1985, **24A**, 1021; 1986, **25A**, 578, 908; *Oxid. Commun.*, 1987, **10**, 31.

8 B. T. Gowda and B. S. Sherigara, *Oxid. Commun.*, 1986, **9**, 165; *Indian J. Chem.*, 1986, **25A**, 960; 1988, **27A**, in the press.

9 B. T. Gowda and J. I. Bhat, *Indian J. Chem.*, 1986, **25A**, 1129, 1149; 1987, **26A**, 215; *J. Indian Chem. Soc.*, 1986, **63**, 665; 1987, **64**, 150; *React. Kinet. Catal. Lett.*, 1986, **31**, 461.

10 J. C. Morris, J. A. Salazar, and M. A. Wineman, *J. Am. Chem. Soc.*, 1948, **70**, 2041.

11 T. J. Jacob and C. G. R. Nair, *Talanta*, 1972, **19**, 347.

12 C. G. R. Nair and P. Indrasenan, *Talanta*, 1976, **23**, 239.

13 C. G. R. Nair, R. L. Kumari, and P. Indrasenan, *Talanta*, 1978, **25**, 525.

14 F. Feigl, 'Spot Tests in Inorganic Analysis,' Elsevier, Amsterdam, 1958.

15 E. A. Werner, *J. Chem. Soc.*, 1923, **123**, 2577.

16 D. Van Nostrand, 'International Encyclopedia of Chemical Science,' Van Nostrand, New York, 1964.

17 E. Schulek, *Z. Anal. Chem.*, 1923, **62**, 337.

18 A. I. Vogel, 'Quantitative Inorganic Analysis,' Longman, London, 1964.

19 E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.

20 M. M. Campbell and G. Johnson, *Chem. Rev.*, 1978, **78**, 65 and references therein.

21 F. E. Hardy and J. P. Johnston, *J. Chem. Soc., Perkin Trans. 2*, 1973, 742.

22 S. W. Benson, 'The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960.

23 K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, New York, 1965.

24 E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, New York, 1966.

25 S. G. Entelis and R. P. Tiger, 'Reaction Kinetics in the Liquid Phase,' Wiley, New York, 1976.

26 J. E. Quinlan and E. S. Amis, *J. Am. Chem. Soc.*, 1955, **77**, 4187.

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