

Kinetics and mechanism of oxidation of thiocarbohydrazide in the free state and in its metal complex and thiocarbohydrazone by chloramine-T and dichloramine-T

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Abstract. Kinetics of oxidation of thiocarbohydrazide (TCH) in the free state and as its metal complex, and as a hydrazone by chloramine-T (CAT) in aqueous HClO_4 medium, and by dichloramine-T (DCT) in 1:1 (v/v) water-methanol medium in the presence of HClO_4 have been studied. Rates of oxidation of TCH in the free state and in metal complex by CAT were determined. The rate law for the oxidation of TCH at high $[\text{H}^+]$ and for complex oxidations were identical to that for CAT oxidations. The conversion of TCH into its hydrazone changed the order in $[\text{H}^+]$ from a positive to a negative value, probably signalling the change of reaction site. The rate law for oxidation under these conditions was determined. Addition of the reduced product of the oxidants had no effect on the rate of oxidations. Variation in ionic strength of the medium had little positive effect, while decrease in dielectric constant of the medium decreased the rate in both the oxidations. Oxidation processes generally follow a Michaelis-Menten type of mechanism. Constants of the rate limiting steps have been calculated at different temperatures and these constants have been used to calculate the activation parameters from the Arrhenius plots. The proposed mechanisms are supported by investigations with HOCl under identical reaction conditions. Metal complexation of the substrate decreased the reactivity, while conversion of TCH into its hydrazone changed the rate dependence on $[\text{H}^+]$.

Keywords. Thiocarbohydrazide; chloramine-T; oxidation kinetics; oxidation mechanism.

1. Introduction

The chemistry of thiosemicarbazide, its next higher homologue, thiocarbohydrazide, and their derivative hydrazones is of interest due to their biological activity and wide synthetic and analytical applications (Williams 1965; Burns 1968; Kurzer and Wilkinson 1970; Ali and Livingstone 1974; Campbell 1975). They are very good metal-chelating agents. Most of the chemical research with these ligands has been concentrated on the structure and bonding of their metal complexes in the solid state. Very little is known of their properties and reactions in solution. Hence a great deal of work remains to be done before one can start rationalising the role of metal-thiosemicarbazide/thiocarbohydrazide/their hydrazones in the pharmacological field. In an effort to provide an insight into the mechanism of their activity in solution the

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kinetics of oxidation of thiosemicarbazide in the free state, and as its metal complex, by three N-halo aromatic sulphonamides have been studied in our laboratory (Gowda and Bhat 1987; Gowda and Rao 1988). In continuation of the efforts in this direction, we report herein the kinetics of oxidation of thiocarbohydrazide in the free state and as its metal complex, and its hydrazone, *bis*-ethylidene thiocarbohydrazide by chloramine-T in aqueous perchloric acid medium, and by dichloramine-T in 1:1 (v/v) water-methanol medium, in the presence of perchloric acid.

2. Materials and methods

Analytical grade chloramine-T (CAT) (Fluka, AG) was used. Dichloramine-T (DCT) was prepared by the chlorination of aqueous CAT solution (Jacob and Nair 1972). The purity of the oxidants was checked by iodometric estimation of the active halogen present in them. A stock solution ($\sim 0.1 \text{ mol dm}^{-3}$) of CAT in water and DCT in methanol were prepared, standardised by the iodometric method and stored in dark-coloured bottles.

Thiocarbohydrazide (TCH) was prepared (Burns 1968) by adding carbondisulphide (15 ml) dropwise with stirring over a period of 1 h to a warm solution ($\sim 50^\circ$) of hydrazine hydrate (50 ml) and water (50 ml) and the resulting mixture being refluxed at 90° for a further period of one hour. The colourless crystals separating out were recrystallised from water. The recrystallised sample melted with decomposition at 168° . Thiocarbohydrazide was characterised by recording its IR spectrum and sulphur estimation: %S = 30.2 (theoretical), 30.5 (found).

The complex, *bis*(thiocarbohydrazide) zinc (II) chloride was prepared (Burns 1968) by mixing warm solutions of zinc chloride in dimethylformamide-water (5:1 v/v) and thiocarbohydrazide in dimethylformamide, in an approximately 1:2 molar ratio. The colourless crystals of the metal complex separated from the solution on standing for 1 h. These were filtered and washed with 0.1 mol dm^{-3} hydrochloric acid, and then dried *in vacuo* over P_2O_5 .

The thiocarbohydrazone, *bis*-ethylidene thiocarbohydrazide was prepared (Guha and De 1935) by adding 50% excess of acetaldehyde in ethanol to a solution of thiocarbohydrazide in 1 mol dm^{-3} acetic acid and refluxing the resulting mixture for one hour. The pale yellow crystals which separated out were recrystallised from dimethylformamide. The crystalline sample melted at $244-6^\circ\text{C}$. The compound was further characterised by recording its spectrum and determining its sulphur content, %S = 20.2 (theoretical), 19.5 (found).

Stock solutions of TCH, its metal complex and hydrazone were prepared in 0.1 mol dm^{-3} aqueous perchloric acid as their aqueous solutions were unstable and decomposed on standing. In the presence of HClO_4 the solutions were stable for several days. The ionic strength of the reaction medium was kept at 0.40 mol dm^{-3} with a concentrated aqueous solution of sodium perchlorate (E Merck). All other chemicals employed were of analytical grade.

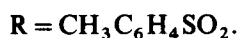
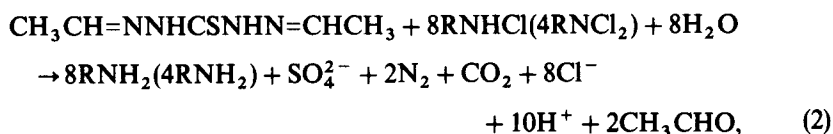
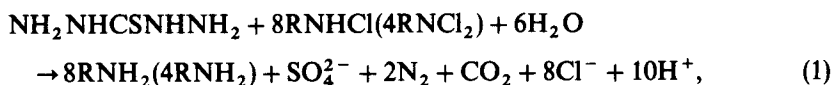
2.1 Kinetic measurements

The kinetic runs were made in glass-stoppered pyrex boiling tubes under pseudo-first order conditions with [substrate] (TCH/its complex/hydrazone) \gg [oxidant] (5- to

20-fold excess). The reactions were initiated by the quick addition of requisite amounts of oxidant solution, thermally equilibrated at a desired temperature, to mixtures containing known amounts of the substrate, perchloric acid and sodium perchlorate solutions and water (methanol with DCT to maintain 50% (v/v) solvent composition), preequilibrated at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric estimation of unreacted oxidants at regular intervals of time. The pseudo-first order rate constants were computed by the method of least squares and the values were reproducible within $\pm 3\%$ error.

2.2 Stoichiometry and product analysis

The stoichiometries of TCH-CAT and TCH-DCT reactions in the free state and as metal complexes, and the hydrazone-CAT(DCT) reactions were determined by allowing the reactions to proceed to completion at 303 K, at different $[H^+]$ (0.01 to 0.20 mol dm⁻³), solvent compositions and [substrate]/[oxidant] ratios. The products, sulphate and carbon dioxide were detected by standard tests (Feigl 1958; *International encyclopedia of chemical sciences* 1976). Further, the sulphate content was estimated by gravimetric methods (Vogel 1964). Yields were $95 \pm 3\%$. *p*-Toluene-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 stoichiometries may be represented as follows,



3. Results

The kinetics of oxidation of TCH, its zinc complex and its hydrazone by CAT in aqueous perchloric acid medium and by DCT in 1:1 water-methanol medium, in the presence of perchloric acid, were studied at several initial concentrations of the substrates, oxidants and HClO₄ (0.02–0.2 mol dm⁻³). The results are shown in tables 1 to 5 and figures 1 to 3. At fixed [substrate] (several-fold excess over the oxidant concentration) and [HClO₄], the plots of $\log[\text{oxidant}]_0/[\text{oxidant}]$ versus time were linear for two half-lives with all the substrates for both the oxidants. The pseudo-first order rate constants (k_{obs}) computed from the plots were unaffected by the changes in $[\text{oxidant}]_0$, establishing first-order kinetics in $[\text{oxidant}]$ in all cases. At fixed $[\text{oxidant}]_0$ and [HClO₄], the rates increased with increase in [TCH], [complex] or [hydrazone]. The plots of $\log k_{\text{obs}}$ versus $\log[\text{TCH}]$, $\log[\text{complex}]$ or $\log[\text{hydrazone}]$ were linear with slopes less than unity in all cases except for DCT

Table 1. Pseudo-first order rate constants (k_{obs}) for the oxidation of thiocarbohydrazide (TCH) and $\text{Zn}(\text{TCH})_2\text{Cl}_2$ complex by chloramine-T (CAT). $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 283 K

$10^3[\text{CAT}]_0$ (mol dm^{-3})	$10^2[\text{TCH}]^*$ or $10^2[\text{complex}]$ (mol dm^{-3})	$10[\text{HClO}_4]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
<i>Effect of varying $[\text{CAT}]_0$</i>			
0.2	1.0	1.0	7.9
0.5	1.0	1.0	7.7
1.0	1.0	1.0	8.3
2.0	1.0	1.0	8.4
<i>Effect of varying $[\text{TCH}]_0$</i>			
1.0	0.5	1.0	4.6
1.0	1.0	1.0	8.3
1.0	2.0	1.0	12.0
1.0	4.0	1.0	16.2
1.0	6.0	1.0	20.2
<i>Effect of varying $[\text{HClO}_4]$</i>			
1.0	1.0	0.2	4.6
1.0	1.0	0.4	5.2
1.0	1.0	0.5	6.2
1.0	1.0	1.0	8.3
1.0	1.0	2.0	11.2
<i>Effect of varying $[\text{CAT}]_0$</i>			
0.25	1.0	1.0	12.3
0.5	1.0	1.0	12.3
1.0	1.0	1.0	12.8
2.0	1.0	1.0	12.8
<i>Effect of varying $[\text{complex}]_0$</i>			
1.0	0.5	1.0	7.2
1.0	1.0	1.0	12.8
1.0	2.0	1.0	19.7
1.0	4.0	1.0	29.1
<i>Effect of varying $[\text{HClO}_4]$</i>			
1.0	1.0	0.4	8.4
1.0	1.0	0.7	10.9
1.0	1.0	1.0	12.8
1.0	1.0	2.2	19.9

* $10^2[\text{TCH}]$ applies to the first 3 sets of data, while $10^2[\text{complex}]$ is for the last 3 sets.

oxidation of TCH at low $[\text{H}^+]$ in which case first-order dependence was observed (table 5). The plots of k_{obs} versus $[\text{TCH}]$, $[\text{complex}]$ or $[\text{hydrazone}]$ attained the limiting values (figure 1), but the double reciprocal plots were linear (figure 2), indicating the operation of Michaelis-Menten type mechanisms. The metal complexation of the ligand TCH decreased the rates of oxidations with both the oxidants, but it had little effect on the kinetic orders.

At constant $[\text{oxidant}]_0$ and $[\text{substrate}]_0$, the rates increased with increase in $[\text{HClO}_4]$ for TCH and complex oxidations with $[\text{CAT}]$ and for the complex

Table 2. Pseudo-first order rate constants (k_{obs}) for the oxidation of thiocarbohydrazide (TCH) and $\text{Zn}(\text{TCH})_2\text{Cl}_2$ complex by dichloramine-T (DCT) in 1:1 (v/v) water-methanol medium. $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K

$10^4 [\text{DCT}]_0$ (mol dm^{-3})	$10^2 [\text{TCH}]^*$ or $10^2 [\text{complex}]$ (mol dm^{-3})	$10^2 [\text{HClO}_4]$ (mol dm^{-3})	$10^2 k_{\text{obs}}$ (s^{-1})
<i>Effect of varying $[\text{DCT}]_0$</i>			
2.5	1.0	1.0	9.9
5.0	1.0	1.0	10.0
10.0	1.0	1.0	10.3
20.0	1.0	1.0	10.1
2.5	1.0	10.0	9.6
5.0	1.0	10.0	10.2
10.0	1.0	10.0	10.2
20.0	1.0	10.0	10.4
<i>Effect of varying $[\text{TCH}]$</i>			
5.0	0.5	1.0	6.0
5.0	1.0	1.0	10.0
5.0	2.0	1.0	28.7
5.0	5.0	1.0	71.0
5.0	0.5	10.0	6.2
5.0	1.0	10.0	10.2
5.0	2.0	10.0	16.2
5.0	5.0	10.0	25.0
<i>Effect of varying $[\text{HClO}_4]$</i>			
5.0	1.0	0.5	18.2
5.0	1.0	1.0	10.0
5.0	1.0	2.0	9.2
5.0	1.0	5.0	6.9
5.0	1.0	10.0	10.2
5.0	1.0	20.0	13.8
<i>Effect of varying $[\text{DCT}]_0$</i>			
0.25	0.5	0.5	7.5
0.5	0.5	0.5	7.5
1.0	0.5	0.5	7.8
2.0	0.5	0.5	7.8
<i>Effect of varying $[\text{complex}]_0$</i>			
0.5	0.3	0.5	4.7
0.5	1.0	0.5	16.4
0.5	2.0	0.5	30.7
<i>Effect of varying $[\text{HClO}_4]$</i>			
0.5	0.5	0.2	5.5
0.5	0.5	0.5	7.5
0.5	0.5	1.0	12.9
0.5	0.5	2.0	16.9

* As in table 1.

Table 3. Pseudo-first order rate constants (k_{obs}) for the oxidation of diacetylidine thiocarbohydrazone by CAT (aqueous medium) and DCT in 1:1 (v/v) water-methanol medium.

$\mu = 0.3 \text{ mol dm}^{-3}$, temperature 283 K

$10^3[\text{CAT}]_0^*$ or $10^4[\text{DCT}]_0$ (mol dm^{-3})	$10^2[\text{Hydrazone}]_0$ (mol dm^{-3})	$10[\text{HClO}_4]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
<i>Effect of varying $[\text{CAT}]_0$</i>			
0.25	1.0	0.5	9.9
0.5	1.0	0.5	9.9
1.0	1.0	0.5	10.3
2.0	1.0	0.5	10.7
<i>Effect of varying $[\text{hydrazone}]_0$</i>			
1.0	0.5	0.5	6.3
1.0	1.0	0.5	10.3
1.0	2.0	0.5	16.0
1.0	4.0	0.5	26.1
<i>Effect of varying $[\text{HClO}_4]$</i>			
1.0	1.0	0.2	14.0
1.0	1.0	0.5	10.3
1.0	1.0	1.0	7.3
1.0	1.0	2.0	6.1
<i>Effect of varying $[\text{DCT}]_0$</i>			
0.10	0.5	0.5	7.4
0.25	0.5	0.5	7.4
0.50	0.5	0.5	7.3
1.0	0.5	0.5	7.3
<i>Effect of varying $[\text{hydrazone}]_0$</i>			
0.5	0.2	0.5	4.8
0.5	0.5	0.5	7.4
0.5	1.0	0.5	12.1
0.5	2.0	0.5	19.9
0.5	4.0	0.5	25.8
<i>Effect of varying $[\text{HClO}_4]$</i>			
0.5	0.5	0.1	12.1
0.5	0.5	0.2	10.1
0.5	0.5	0.5	7.4
0.5	0.5	1.0	5.9
0.5	0.5	2.0	4.9

* $10^3[\text{CAT}]_0$ applies for the first 3 sets of data and $10^4[\text{DCT}]_0$ for the last three sets.

oxidation with DCT (tables 1 and 2). The plots of $\log k_{\text{obs}}$ versus $\log [\text{HClO}_4]$ were linear with slopes < 1 (table 5). For the oxidation of TCH by DCT, the rate first decreased with increase in $[\text{HClO}_4]$ up to 0.05 mol dm^{-3} and increased thereafter (table 2). The kinetic orders in $[\text{TCH}]$ were determined in both the ranges of $[\text{HClO}_4]$ (table 5). The rates decreased with increase in $[\text{HClO}_4]$ for the hydrazone oxidations with both the oxidants over the entire range of $[\text{HClO}_4]$ (table 3). The log-log plots were linear with slopes < -1 (table 5), indicating that the mechanisms of oxidation with TCH and hydrazone are different, i.e., the sites of attack are different.

Table 4. Effects of varying ionic strength and dielectric constant of the reaction media and addition of the reaction product, PTS on the rates of oxidations of thiocarbohydrazide (TCH) by CAT (aqueous medium) at 283 K and DCT in 1:1 (v/v) methanol-water medium at 293 K.

$\mu = 0.4 \text{ mol dm}^{-3}$

	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
	CAT ^a	DCT ^b
$\mu (\text{mol dm}^{-3})$		
0.2	7.8	9.8
0.3	8.3	10.1
0.4	8.4	10.2
0.5	8.6	10.6
$10^3 [\text{PTS}] (\text{mol dm}^{-3})$		
1.0	8.3	10.1
2.0	8.1	10.2
4.0	8.0	10.1
8.0	8.0	10.2
% Methanol by volume		
10	7.3	—
20	6.8	18.1
30	6.3	12.8
50	—	10.2
60	—	9.8

^a $10^3 [\text{CAT}]_0 = 10^2 [\text{TCH}]_0 = 10 [\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$.

^b $10^4 [\text{DCT}]_0 = 5.0 \text{ mol dm}^{-3}$, $10^2 [\text{TCH}]_0 = 10 [\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$.

Table 5. Comparison of kinetic data for the oxidation of thiocarbohydrazide (TCH) and thiosemicarbazide (TSC) by chloramine-T (CAT), dichloramine-T (DCT), chloramine-B (CAB), dichloramine-B (DCB) and hypochlorite in acid medium.

Order observed in	(i) Oxidation of TCH in the free state and as its metal complex and hydrazone						
	CAT			DCT			NaOCl
	TCH	Complex	Hydrazone	TCH ^a	Complex	Hydrazone	TCH
[Oxidant]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[TCH]	0.6	0.6	0.7	0.6(1.0)	~1.0	0.5	0.6
[H ⁺]	0.35	0.5	-0.4	0.5(-0.3)	0.5	-0.3	0.22
	(ii) Oxidation of TSC in the free state						
	CAT	DCT	CAB	DCB	NaOCl		
[Oxidant]	1.0	1.0	1.0	1.0	1.0		
[TSC]	0.4	0.3	0.28	0	0.25		
[H ⁺]	-0.7	-1.0	-0.95	-0.8	-0.7		

^a Values in parentheses are at low [H⁺].

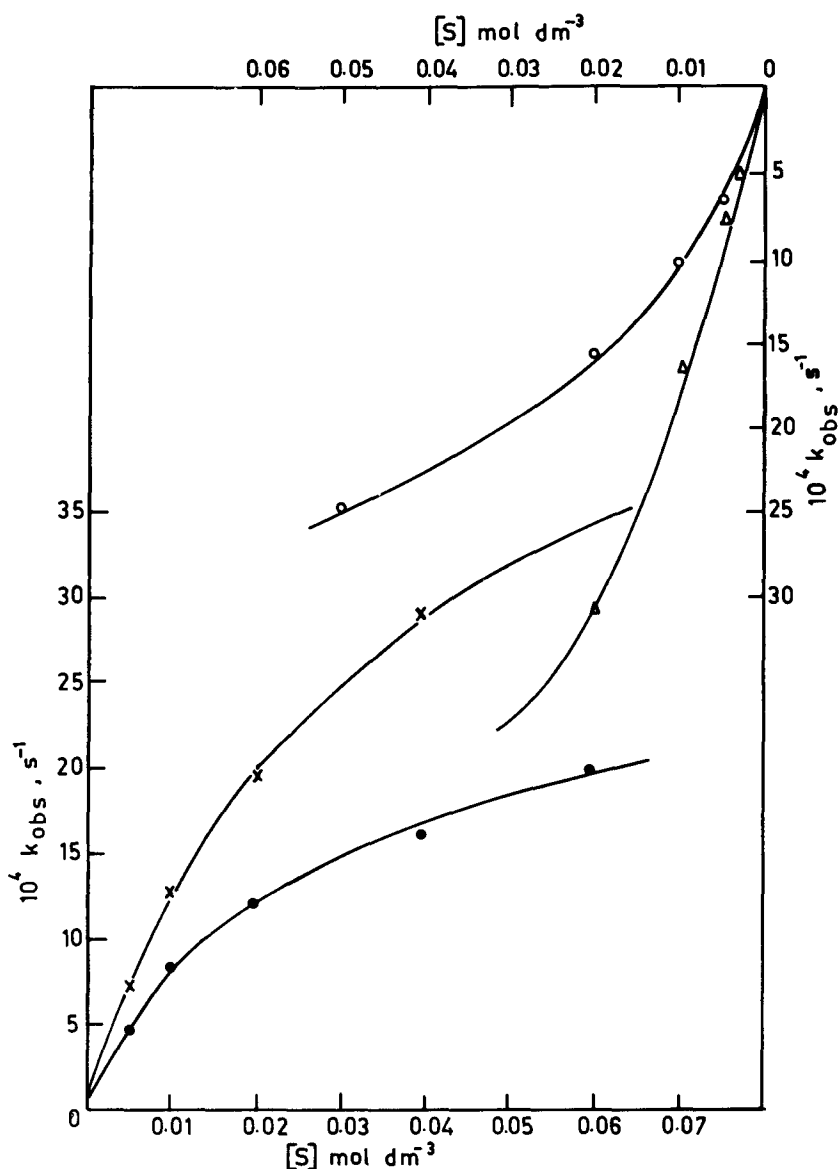


Figure 1. Plots of k_{obs} versus $[S]$, ● TCH, × complex. $10^3[\text{CAT}]_0 = 10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 283 K. ○ TCH: $10^4[\text{DCT}]_0 = 5.0 \text{ mol dm}^{-3}$, $10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K. △ complex: $10^4[\text{DCT}]_0 = 10^2[\text{HClO}_4] = 5.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K.

Addition of the reduced product of the oxidants, *p*-toluene-sulphonamide, to the reaction mixtures had no significant effect on the rates of oxidations with both the oxidants (table 4). Variation in ionic strength of the medium had little positive effect on the rates of reactions, while the decrease in dielectric constant of the medium decreased the rate in both cases (table 4).

Substrate concentrations were varied at different temperatures. Activation

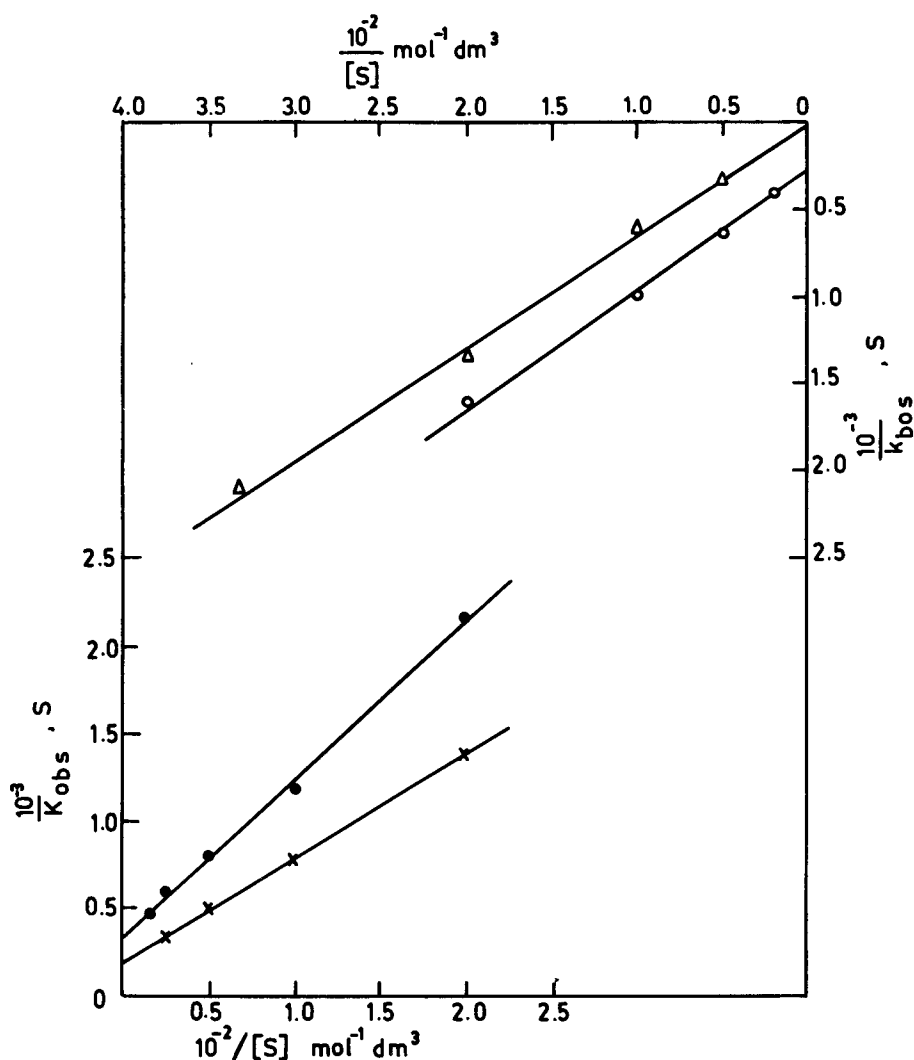


Figure 2. Plots of $1/k_{\text{obs}}$ versus $1/[S]$, \circ TCH, \times complex. $10^3[\text{CAT}]_0 = 10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 283 K. \bullet TCH: $10^4[\text{DCT}]_0 = 5.0 \text{ mol dm}^{-3}$, $10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K. Δ complex: $10^4[\text{DCT}]_0 = 10^2[\text{HClO}_4] = 5.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K.

parameters have been calculated from the rate coefficients of the rate limiting steps. The latter were calculated as described under discussion.

4. Discussion

Chloramine-T (N-chloro-N-sodio-*p*-toluene-sulphonamide, RNCINa , where $\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$) is a moderately strong electrolyte in aqueous solutions, and it furnishes different reactive species in aqueous solutions depending upon the pH of the reaction medium (Bishop and Jennings 1958; Campbell and Johnson 1978; Gowda

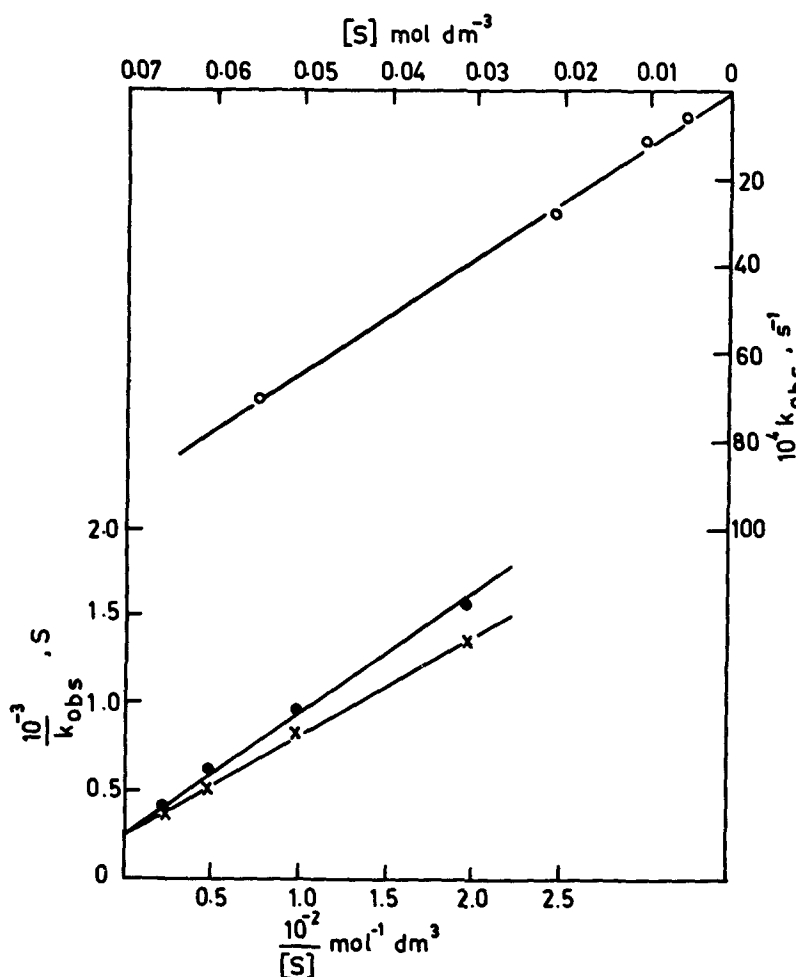
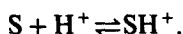


Figure 3. (i) Plots of $1/k_{\text{obs}}$ versus $1/[S]$ (hydrazone). ○ $10^3[\text{CAT}]_0 = 20[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.3 \text{ mol dm}^{-3}$, temperature 283 K. × $10^4[\text{DCT}]_0 = 10^2[\text{HClO}_4] = 5.0 \text{ mol dm}^{-3}$, $\mu = 0.3 \text{ mol dm}^{-3}$, temperature 283 K. (ii) Plot of k_{obs} versus $[S]$ (TCH) ● $10^4[\text{DCT}]_0 = 5.0 \text{ mol dm}^{-3}$, $10^2[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, temperature 293 K.

and Mahadevappa 1983). The probable reactive species in aqueous solutions of CAT and partial aqueous solutions of DCT are RNHCl , RNCl_2 and HOCl at low $[\text{H}^+]$ and $(\text{RNH}_2\text{Cl})^+$, $(\text{RNCl}_2\text{H})^+$ and $(\text{H}_2\text{OCl})^+$ at high $[\text{H}^+]$.

In acid solutions that following protonation equilibrium exists for the ligand thiocarbohydrazide (S),

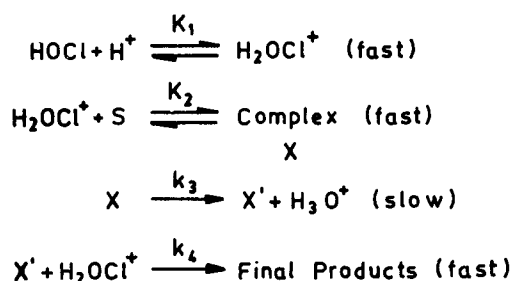


Under strong acidic conditions the substrate exists mostly in the protonated form.

5. Mechanism of oxidation

5.1 Oxidation of TCH by CAT

The kinetics of first order in [CAT] and fractional order in both [TCH] and $[H^+]$, observed for the oxidation of TCH both in the free state and as the metal complex may be explained by a Michaelis–Menten type mechanism (scheme 1). Under the present experimental conditions with $[H^+]$ around 0.01 mol dm^{-3} , the terminal $-NH_2$ groups get protonated and thus are difficult to oxidise. Hence the $-SH$ group formed from the isomerisation of TCH is the initial attacking point.



Scheme 1

Based on scheme 1, rate law (3) has been deduced

$$-\frac{d[\text{CAT}]}{dt} = \frac{K_1 K_2 k_3 [\text{CAT}]_{\text{tot}} [\text{S}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{S}] [\text{H}^+]}, \quad (3)$$

or

$$k_{\text{obs}} = \frac{K_1 K_2 k_3 [\text{S}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{S}] [\text{H}^+]}, \quad (4)$$

or

$$\frac{1}{k_{\text{obs}}} = \left\{ \frac{1 + K_1 [\text{H}^+]}{K_1 K_2 k_3 [\text{H}^+]} \right\} \frac{1}{[\text{S}]} + \frac{1}{k_3}. \quad (5)$$

The plot of $1/k_{\text{obs}}$ versus $1/[\text{S}]$ is linear with a finite intercept on the ordinate, both in the free state and as the metal complex, in accordance with the rate law (5) (figure 2). The reciprocal of the intercept gives the rate constant (k_3) of the rate-determining step. This constant was calculated at different temperatures (278–298 K) by varying [TCH] at each temperature. The latter constants were used to compute the activation parameters from the Arrhenius plots, $\log k_3$ versus $1/T$ and $\log(k_3 T)$ versus $1/T$. The values are 76.1 kJ mol^{-1} , 11.4 , 73.7 kJ mol^{-1} , $-34.0 \text{ JK}^{-1} \text{ mol}^{-1}$ and 83.3 kJ mol^{-1} for E_a , $\log A$, ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , respectively.

A detailed mechanism of oxidation is shown in scheme 2.

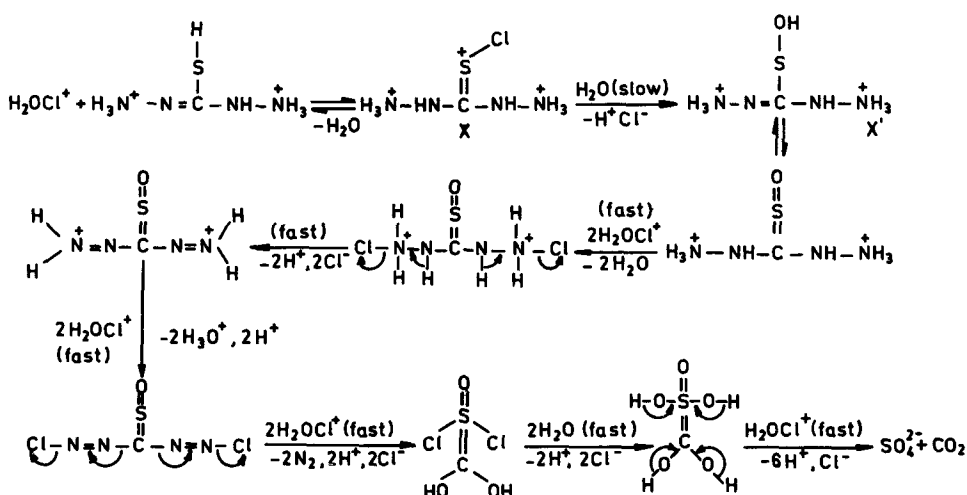


Table 6. Pseudo-first order rate constant (k_{obs}) for the oxidation of thiohydrazide by hypochlorous acid as $[\text{HOCl}]_0$, $[\text{TCH}]_0$ and $[\text{HClO}_4]$ are varied.
 $\mu = 0.3 \text{ mol dm}^{-3}$, temperature 283 K

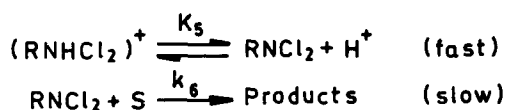
$10^3 [\text{HOCl}]_0$ (mol dm^{-3})	$10^2 [\text{TCH}]_0$ (mol dm^{-3})	$10 [\text{HClO}_4]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
<i>Effect of varying $[\text{HOCl}]_0$</i>			
0.25	1.0	1.0	6.9
0.50	1.0	1.0	7.0
1.0	1.0	1.0	7.0
2.0	1.0	1.0	7.0
<i>Effect of varying $[\text{TCH}]_0$</i>			
1.0	0.5	1.0	4.3
1.0	1.0	1.0	7.0
1.0	2.0	1.0	9.0
1.0	4.0	1.0	16.5
<i>Effect of varying $[\text{HClO}_4]$</i>			
1.0	1.0	0.2	4.8
1.0	1.0	0.5	5.5
1.0	1.0	1.0	7.0
1.0	1.0	2.0	8.0

The proposed mechanism envisages the participation of HOCl, and hence H_2OCl^+ as the reactive species, formed from the decomposition of chloramine-T. This has been verified independently by investigating the kinetics of the oxidation reaction between TCH and HOCl under identical reaction conditions. A typical set of data is shown in table 6. Identical kinetics observed in HOCl oxidations provide additional support to the suggested mechanism.

5.2 Oxidation of TCH by DCT

In DCT oxidations, kinetic order in $[H^+]$ is dependent on its concentrations. It is inverse fractional order at low $[H^+]$ (up to 0.05 mol dm^{-3}) and fractional order at high $[H^+]$ ($> 0.04 \text{ mol dm}^{-3}$). The rate also follows first-and fractional-order kinetics in $[TCH]$ at low and high $[H^+]$ respectively. But the oxidation is first order in $[DCT]$ under both the conditions.

5.2a At low $[HClO_4]$ ($< 0.05 \text{ mol dm}^{-3}$): The kinetics of first order each in $[DCT]$ and $[TCH]$ and inverse fractional order in $[H^+]$ and the observed non-influence of the reaction product PTS can be explained by scheme 3.



Scheme 3

Application of steady state hypothesis to the intermediate with the assumption that the k_6 term in the denominator is negligible and $[RNHCl_2^+] = [RNHCl_2^+]_0 - [RNCl_2] = [DCT] = [DCT]_0 - [RNCl_2]$ leads to the rate law (13)

$$-\frac{d[DCT]}{dt} = \frac{K_5 k_6 [DCT]_0 [S]}{K_5 + [H^+]}, \quad (6)$$

or

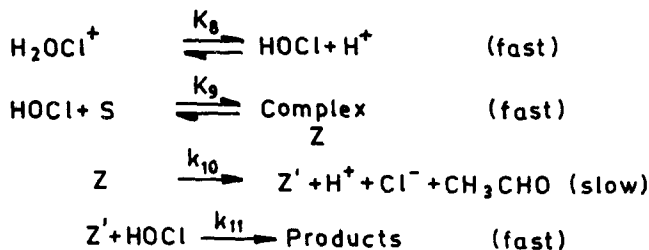
$$k_{\text{obs}} = \frac{K_5 k_6 [S]}{K_5 + [H^+]}. \quad (7)$$

Plot of k_{obs} versus $[S]$ is linear with the intercept equal to zero on the ordinate (figure 3) in conformity with rate law (7).

5.2b At high $[HClO_4]$ ($> 0.04 \text{ mol dm}^{-3}$): Under these conditions the rate follows first-order kinetics in $[DCT]$ and fractional-order in $[TCH]$ and $[H^+]$, i.e., the rate dependence in $[TCH]$ changes from first order to fractional order and that in $[H^+]$ from inverse fractional to fractional order. At low $[H^+]$ terminal NH_2 groups are likely to be attacked by the oxidant. But at high $[H^+]$ these NH_2 groups get protonated and hence are difficult to approach since the protonated species are more difficult to oxidise than the unprotonated forms. Hence at high $[HClO_4]$, protonated TCH is likely to be attacked. The decrease in dependence of rate on $[TCH]$ as $[H^+]$ increases also indicates that the reaction site under high acid conditions is different. H_2OCl^+ or $RNHCl_2^+$ are the probable oxidising species under these conditions. The kinetics under high acid conditions are similar to CAT kinetics and may be explained by scheme 1 and rate laws (3)–(5). The plot of $1/k_{\text{obs}}$ versus $1/[S]$ is linear even under these conditions with a finite intercept on the ordinate in accordance with rate law (5), for both TCH and its metal-complex oxidations (figure 2). The constant k_3 was calculated (from the intercept of the plot) at different temperatures (283–293 K) by varying $[TCH]$ at each temperature. These constants have been used to compute the activation parameters from the Arrhenius plots. The values are 59.9 kJ mol^{-1} , 8.4 , 57.5 kJ mol^{-1} , $-93.1 \text{ JK}^{-1} \text{ mol}^{-1}$ and 84.7 kJ mol^{-1} for E_a , $\log A$, ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger , respectively.

5.3 Oxidation of hydrazone by CAT and DCT

It is interesting to note that the hydrazone had significantly different kinetics. The dependence of rate on $[H^+]$ changed from fractional order to inverse fractional order in both CAT and DCT oxidations, on conversion of TCH into the hydrazone. The kinetics of first order in [oxidant], fractional order in [hydrazone] and inverse fractional order in $[H^+]$ can be explained on the basis of scheme 4 (where S denotes hydrazone).



Scheme 4

The rate laws (8)–(10) in accordance with scheme 4 have been obtained by a method similar to the derivation of earlier equations.

$$-\frac{d[OX]}{dt} = \frac{K_8 K_9 k_{10} [\text{oxidant}]_{\text{tot}} [S]}{K_8 + [H^+] + K_8 K_9 [S]} \quad (8)$$

or

$$k_{\text{obs}} = \frac{K_8 K_9 k_{10} [S]}{K_8 + [H^+] + K_8 K_9 [S]} \quad (9)$$

or

$$\frac{1}{k_{\text{obs}}} = \left\{ \frac{K_8 + [H^+]}{K_8 K_9 k_{10}} \right\} \frac{1}{[S]} + \frac{1}{k_{10}} \quad (10)$$

The rate law (10) predicts linearity between $1/k_{\text{obs}}$ and $1/[S]$. The plot of $1/k_{\text{obs}}$ versus $1/[S]$ is linear with finite intercept in both the oxidations, in conformity with predictions (figure 3). The constant k_{10} was calculated from the intercepts

$$(10^4)k_{10} \text{ s}^{-1} = 38.5 (\text{CAT}), 40.7 (\text{DCT}).$$

The kinetic evidence of change of rate dependence in $[H^+]$ from fractional order to inverse fractional order on conversion of TCH into its hydrazone indicates the change of reaction site. If the $-SH$ group formed from the isomerisation of hydrazone continued to be the reaction site, one would expect a positive dependence on $[H^+]$ even under these conditions. Results observed contrary to expectations indicate that the reaction site is different. It is likely that HOCl is added across $C=N$, in the pre-equilibrium step, to form an intermediate, which subsequently undergoes disproportionation in the rate-determining step and then reacts with another seven molecules of HOCl, in fast steps, to give sulphate, CO_2 and acetaldehyde as the final products (scheme 5).

expectations and the kinetics observations in hydrazone oxidations establish that the –SH group formed from the thione sulphur is the attacking point. These results are further supported by investigations with HOCl (table 6).

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References

- Ali M A and Livingstone S E 1974 *Coord. Chem. Rev.* **13** 101
Amis E S 1966 *Solvent effects on reaction rates and mechanisms* (New York: Academic Press)
Bishop E and Jennings V J 1958 *Talanta* **1** 197
Burns G R 1968 *Inorg. Chem.* **7** 277
Campbell M J M 1975 *Coord. Chem. Rev.* **15** 279
Campbell M M and Johnson G 1978 *Chem. Rev.* **78** 65
Entelis S G and Tiger R P 1976 *Reaction kinetics in the liquid phase* (New York: Wiley)
Feigl F 1958 *Spot tests in inorganic analysis* (Amsterdam: Elsevier)
Gowda B T and Bhat J I 1987 *Tetrahedron* **43** 2119
Gowda B T and Mahadevappa D S 1983 *J. Chem. Soc., Perkin 2* 323
Gowda B T and Rao R V 1988 *J. Chem. Soc., Perkin 2* 355
Guha P C and De S C 1935 *J. Indian Chem. Soc.* **2** 225
International encyclopedia of chemical sciences 1976 (New York: D Van Nostrand)
Jacob T J and Nair C G R 1972 *Talanta* **19** 347
Kurzer I and Wilkinson M 1970 *Chem. Rev.* **70** 111
Laidler K J 1987 *Chemical kinetics* (New York: Harper and Row)
Vogel A I 1964 *Quantitative inorganic analysis* (London: Longmans)
Williams J F 1965 *Fortschr. Chem. Forsch.* **5** 147
Zuman P and Patel R 1984 *Techniques in organic reaction kinetics* (New York: Wiley)