

Kinetics and mechanism of oxidation of carbohydrazide and thiocarbohydrazide by N-bromoacetamide

B THIMME GOWDA* and P JAGAN MOHANA RAO

Department of Post-Graduate Studies and Research in Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India

MS received 27 May 1989; revised 23 October 1989

Abstract. Kinetics of oxidation of carbohydrazide (ch) by N-bromoacetamide (NBA) in aqueous perchloric acid medium and thiocarbohydrazide (tch) in the free state and in its metal complex by NBA both in the presence and absence of added bromide ion have been investigated in aqueous perchloric acid medium. Oxidation of carbohydrazide showed first order kinetics in [NBA], nearly first order in [ch] and inverse fractional order in $[H^+]$. The rate slightly decreased with increase in ionic strength of the medium. Addition of either the reduced product of the oxidant or bromide had no significant effect on the rate of CH oxidation. Oxidation of thiocarbohydrazide in the free and metal-bound states both in the presence and absence of added bromide showed first order kinetics in [NBA] and fractional order in both [tch] and $[H^+]$. But the fractional order in $[H^+]$ for the oxidation of tch in the presence of Br^- was almost twice that in its absence. The rate increased with increase in $[Br^-]$ with a fractional order of about 0.3. Variation in ionic strength of the medium had very negligible effects. Addition of acetamide, the reduced product of the oxidant, had no effect on the rate. Michaelis–Menten type mechanisms have been considered to explain the observed results. Activation parameters have been computed for all the oxidations by measuring rates at different temperatures. Detailed mechanisms of oxidations have also been suggested.

Keywords. Kinetics and mechanism; oxidation; carbohydrazide; thiocarbohydrazide; N-bromoacetamide.

1. Introduction

Carbohydrazide ($H_2NHNCONHNH_2$) (ch) is the final member of the structural sequence; urea, semicarbazide and carbohydrazide (Kurzer and Wilkinson 1970). It is a hydrazine derivative of carbonic acid. Both hydrazine groups of carbohydrazide display normal reactivity toward carbonyl compounds and give rise to a large number of crystalline mono- and dihydrazones. Thiocarbohydrazide ($H_2NHNCSNHNH_2$) (tch) is a member of the other structural sequence; thiourea, thiosemicarbazide and thiocarbohydrazide (Kurzer and Wilkinson 1970). The chemical behaviour of thiocarbohydrazide is similar to its keto analogue carbohydrazide. Thiocarbohydrazides possess anticarcinogenic and antibacterial properties. The parent compound exhibits a toxicity towards the housefly comparable to that of DDT. It also shows fungicidal

*For correspondence

properties and has been tested against different species. Although the two substrates have been extensively used as metal chelating agents (Burns 1968; Kurzer and Wilkinson 1970; Ali and Livingstan 1974; Campbell 1978), there are no reports on the mechanistic aspect of their reactions in solution.

As a part of our mechanistic investigations of reactions of biologically active substrates in the liquid phase (Gowda and Bhat 1987–1989; Gowda and Rao 1988; Gowda and Ramachandra 1989; Gowda and Rao 1989; Gowda and Sherigara 1987, 1989), we report herein the kinetics of oxidations of carbohydrazide by N-bromoacetamide in aqueous perchloric acid medium and thiocarbohydrazide in the free state and in its metal-bound state, both in the presence and absence of added bromide ions, by N-bromoacetamide in aqueous perchloric acid medium, under varying conditions.

2. Materials and methods

N-bromoacetamide (NBA) was prepared by the bromination of acetamide in 50% KOH (Oliveto and Gerold 1963). Stock solution of the oxidant ($\sim 0.10 \text{ mol dm}^{-3}$) was prepared in double-distilled water, standardised by the iodometric method and preserved in dark-coloured bottles.

Carbohydrazide was prepared by mixing diethylcarbonate and 85% hydrazine hydrate in 1:2:2 molar ratio (Mohr *et al* 1953; Kurzer and Wilkinson 1970). Alcohol and water formed by the exothermic reaction were removed by distillation. The remaining liquid was cooled to 20°C and allowed to stand for at least 1 h. Crystals of carbohydrazide which separated out were filtered and dissolved in hot water. Carbohydrazide was then precipitated out by adding 95% ethanol and allowed to stand for about 1 h at 20°C . The precipitate was filtered and washed with ether. The purity of the compound was checked by determining its melting point (154°) and by nitrogen estimation. Aqueous stock solution (0.5 mol dm^{-3}) of carbohydrazide was used.

Thiocarbohydrazide was prepared by refluxing the mixture of carbon disulphide and hydrazine hydrate at 90° for a period of 1 h (Burns 1968). The colourless crystals which separated out were recrystallised from water. The recrystallised sample melted with decomposition at 168° . Thiocarbohydrazide was also characterised by recording its IR spectrum and by sulphur estimation.

The complex, *bis*(thiocarbohydrazide)zinc(II) chloride was obtained by mixing warm solutions of zinc chloride in dimethyl formamide–water (5:1, v/v) and thiocarbohydrazide in dimethyl formamide, in an approximately 1:2 molar ratio (Burns 1968). The colourless crystals of the metal complex that separated out from the solution on standing for over an hour, were filtered and washed with 0.10 mol dm^{-3} hydrochloric acid and then dried under vacuum over P_2O_5 .

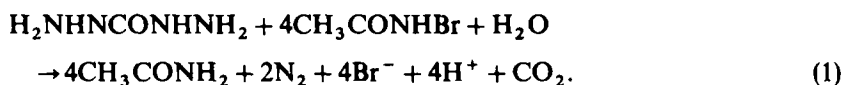
The stock solutions ($\sim 0.05 \text{ mol dm}^{-3}$) of thiocarbohydrazide and its metal complex were prepared in 0.10 mol dm^{-3} aqueous perchloric acid as their aqueous solutions were unstable and decomposed on standing. In aqueous perchloric acid the solutions were stable for several days. All other reagents employed were of accepted grades of purity.

2.1 Kinetic measurements

The kinetic runs were made in glass-stoppered pyrex boiling tubes under pseudo-first order conditions with [substrate] \gg [oxidant] (5–100 fold excess). The reactions were initiated by the quick addition of requisite amounts of oxidant solution (0.0005–0.004 mol dm⁻³), thermally pre-equilibrated at a desired temperature, to solutions containing known amounts of substrate (0.005–0.10 mol dm⁻³) and perchloric acid (0.0005–0.20 mol dm⁻³) thermostatted at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric determination of unreacted oxidant at regular intervals of time. The pseudo-first order rate constants (k_{obs}) were computed by graphical methods and the values were reproducible within $\pm 4\%$ error.

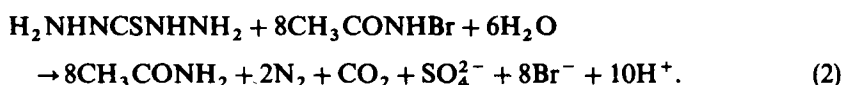
2.2 Stoichiometry and product analysis

The stoichiometries of ch-NBA and tch-NBA reactions were determined by thermally equilibrating varying ratios of reaction mixtures ([NBA] = 4×10^{-3} – 6×10^{-2} mol dm⁻³), [substrate] = 1×10^{-3} mol dm⁻³ at different [HClO₄] (0.001–0.10 mol dm⁻³). Estimation of unreacted oxidant in the reaction mixture showed that one mole of ch reacts with four moles of oxidant. The observed 1:4 stoichiometry may be represented by.



Nitrogen evolved was determined quantitatively by making use of Schiff's nitrometer. A slow and steady current of pure and dry CO₂ was passed through the reaction vessel to sweep off N₂ to the nitrometer filled with 50% KOH, where the CO₂ was completely absorbed. The volume of N₂ was noted and compared with the theoretical value.

Thiocarbohydrazide was found to get oxidised to sulphate to the extent of about $90 \pm 5\%$. Sulphate formed was gravimetrically estimated as barium sulphate.



3. Results

The kinetics of oxidations of (a) carbohydrazide by N-bromoacetamide in aqueous perchloric acid medium and (b) thiocarbohydrazide and its complex by N-bromoacetamide both in the presence and absence of bromide ion in aqueous perchloric acid medium, were studied under varying conditions. The results are shown in tables 1–5 and figures 1 and 2. At fixed [substrate] (several fold excess over [oxidant]) and [HClO₄], the plots of log [NBA] versus time were linear at least for two half-lives for all the substrates. The pseudo-first order rate constants (k_{obs}) computed from the

Table 1. Pseudo-first order rate constants (k_{obs}) for the oxidations of carbohydrazide (ch), thiocarbohydrazide (tch) and its metal complex $[Zn(tch)_2Cl_2]$ by N-bromoacetamide (NBA) in aqueous perchloric acid medium^a at 303 K (ch) and 283 K [tch and $Zn(tch)_2Cl_2$].

		$10^4 k_{obs} (s^{-1})$			
		tch in the			
$10^3 [NBA]_0$ (mol dm ⁻³)	$10^2 [substrate]^b$ (mol dm ⁻³)	ch	presence of Br ^{-c}	absence of Br ⁻	$Zn(tch)_2Cl_2$
<i>Effect of varying [NBA]₀</i>					
0.5	1.0(2.0)	7.7	20.8	13.1	16.8
1.0	1.0(2.0)	7.4	20.3	13.6	17.1
2.0	1.0(2.0)	7.5	21.4	14.1	17.2
3.0	1.0(2.0)	—	22.2	13.7	17.7
4.0	1.0(2.0)	7.8	—	—	—
<i>Effect of varying [substrate]₀</i>					
1.0	0.5	2.3	15.4	9.6	12.5
1.0	1.0	4.3	20.3	13.6	17.1
1.0	2.0	7.4	29.8	17.6	23.1
1.0	3.0	—	—	21.7	28.8
1.0	5.0	19.5	43.5	28.4	32.7
1.0	10.0	36.6	—	—	—

^a $10^2 [HClO_4] (mol dm^{-3}) = 0.3(ch), 5.0[tch, Zn(tch)_2Cl_2]$; ^bvalues in parentheses are for ch; ^c $10^3 [Br^-] = 5.0 mol dm^{-3}$

Table 2. Effect of variation in $[H^+]$ on the rates of oxidations of carbohydrazide (ch), thiocarbohydrazide (tch) and its metal complex $[Zn(tch)_2Cl_2]$ by N-bromoacetamide (NBA) in aqueous perchloric acid medium at 303 K (ch) and 283 K [tch and $Zn(tch)_2Cl_2$].

		$10^4 k_{obs}^d (s^{-1})$			
		tch in the			
$10^3 [HClO_4]$ (mol dm ⁻³)	$10^4 k_{obs}^a$ (s ⁻¹)	$10^2 [HClO_4]$ (mol dm ⁻³)	presence of Br ⁻	absence of Br ⁻	$Zn(tch)_2Cl_2$
0.5	11.1	2.0	16.1	8.8	17.1
1.0	8.7	3.0	13.5	9.6	13.7
2.0	7.9	4.0	17.5	—	—
3.0	7.4	5.0	20.3	13.6	17.3
5.0	6.2	7.5	29.1	—	—
10.0	5.8	10.0	33.4	17.2	22.6
20.0	8.8	20.0	—	24.4	32.5

^a $10^3 [NBA]_0 = 50 [ch]_0 = 1.0 mol dm^{-3}$; ^b $10^3 [NBA]_0 = 10^2 [tch \text{ or complex}]_0 = 1.0 mol dm^{-3}$; ^c $10^3 [Br^-] = 5.0 mol dm^{-3}$.

Table 3. Effect of variation in ionic strength (I), addition of the reaction product—acetamide (AcNH_2), KBr , ZnSO_4 on the rates of oxidations of ch , tch and $\text{Zn}(\text{tch})_2\text{Cl}_2$ by NBA in aqueous perchloric acid medium^a at 303 K (ch) and 283 K [tch and $\text{Zn}(\text{tch})_2\text{Cl}_2$].

$10 \times I$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$							
	$10^4 k_{\text{obs}} (\text{s}^{-1})$			$10^3 [\text{AcNH}_2]$ (mol dm^{-3})	In absence of Br^-			In presence of Br^- tch
	ch	tch	$\text{Zn}(\text{tch})_2\text{Cl}_2$		ch	tch	$\text{Zn}(\text{tch})_2\text{Cl}_2$	
1.0	6.8	12.4	16.0	0.0	7.4	13.6	17.1	20.3
2.0	7.2	—	—	1.0	7.2	14.4	17.8	20.4
3.0	7.4	13.6	17.1	2.0	7.1	—	—	—
5.0	7.6	14.4	17.8	5.0	6.9	15.0	18.9	20.9
$10^3 [\text{KBr}] (\text{mol dm}^{-3})$				$10^2 [\text{ZnSO}_4] (\text{mol dm}^{-3})$				
1.0	6.9	14.4		1.0	7.4			
2.0	6.9	15.9		2.0	7.3			
5.0	7.1	20.3		5.0	7.5			
10.0	7.0	25.2						
20.0	6.9	38.9						

^a $10^3 [\text{NBA}]_0 = 50 [\text{CH}]_0 = 10^2 [\text{tch or complex}]_0 = 1.0 \text{ mol dm}^{-3}$, $10^2 [\text{HClO}_4] (\text{mol dm}^{-3}) = 0.3$ (ch), 5.0 [tch and $\text{Zn}(\text{tch})_2\text{Cl}_2$].

Table 4. Kinetic data and activation parameters for the oxidations of carbohydrazide (ch), thiocarbohydrazide (tch) and its metal complex by N -bromoacetamide (NBA) in aqueous perchloric acid medium.

Orders observed in	In the absence of Br^-			In the presence or Br^-
	ch	tch	$\text{Zn}(\text{tch})_2\text{Cl}_2$	tch
$[\text{NBA}]$	1.0	1.0	1.0	1.0
$[\text{substrate}]$	0.90	0.46	0.44	0.48
$[\text{H}^+]$	-0.22	0.45	0.44	0.81
$[\text{Br}^-]$	—	—	—	0.27
<i>Activation parameters</i>				
	<i>Calcd.^a</i>	<i>Calcd.^b</i>		
$E_a (\text{kJ mol}^{-1})$	63.7	61.1		
$\log A$	8.65	8.73		
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	65.7	63.2		
$\Delta S^\ddagger (\text{JK}^{-1})$	-92.1	-71.7		
$\Delta G^\ddagger (\text{kJ mol}^{-1})$	93.6	83.4		

^aCalculated from k_5 values at different temperatures (see text)

^bCalculated from k_8 values at different temperatures (see text)

plots were unaffected by the changes in $[\text{NBA}]$ (table 1), showing first order kinetics in $[\text{oxidant}]$ in all the cases. At constant $[\text{NBA}]_0$ and $[\text{HClO}_4]$, the rates increased with increase in $[\text{ch}]$ or $[\text{tch}]$ or $[\text{complex}]$. The plots of $\log k_{\text{obs}}$ versus $\log [\text{ch}]$ or $\log [\text{tch}]$ or $\log [\text{complex}]$ were linear with slopes less than unity for all the oxidations

Table 5. Comparison of predicted and experimental rate constants for the oxidation of carbohydrazide in aqueous perchloric acid medium.

$10^4 k(s^{-1})$			
Predicted*			Observed
I	II		
$10^2 [ch]_0 (mol dm^{-3})$			
0.5	2.0	2.3	2.3
1.0	3.9	4.5	4.3
2.0	7.5	8.6	7.4
5.0	16.7	19.1	19.5
10.0	28.0	32.1	36.6
$10^3 [H^+] (mol dm^{-3})$			
0.5	8.4	8.5	11.1
1.0	8.1	8.3	8.7
2.0	7.6	7.9	7.9
3.0	7.3	7.5	7.4
5.0	6.7	6.9	6.2
10.0	5.7	5.7	5.8

*Values predicted from the rate law (5) or (6) (I) and rate law (10) (II) (see text)

(table 4). The plots of k_{obs} versus $[ch]$, $1/k_{obs}$ versus $1/[ch]$, $1/k_{obs}$ versus $1/[tch]$ and $1/k_{obs}$ versus $1/[complex]$ were linear (figures 1 and 2).

The rate for the oxidation of carbohydrazide decreased with increase in $[HClO_4]$, at fixed $[NBA]_0$ and $[ch]_0$, with an inverse fractional order dependence in $[H^+]$. Rates of other oxidations increased with increase in $[HClO_4]$, with fractional order dependences in $[H^+]$. But the rate dependence on $[H^+]$ in the presence of bromide was almost twice as that in its absence.

Variations in ionic strength of the medium had no significant effect on the rates of oxidation. Addition of the reduced product, acetamide to the reaction mixtures had also negligible effects in all the cases (table 3). Addition of zinc sulphate had no effect on the rate of carbohydrazide oxidation.

Rates were measured at different temperatures (278–313 K) and Activation parameters have been calculated from the Arrhenius plots (table 4).

4. Discussion: mechanisms of oxidation

4.1 Oxidation of carbohydrazide

The kinetics of first order in $[NBA]$, fractional order in $[ch]$ and inverse fractional order in $[H^+]$ and the observed lack of influence of the product (acetamide, $AcNH_2$) may be explained by scheme 1. In scheme 1, deprotonation of the oxidant takes place

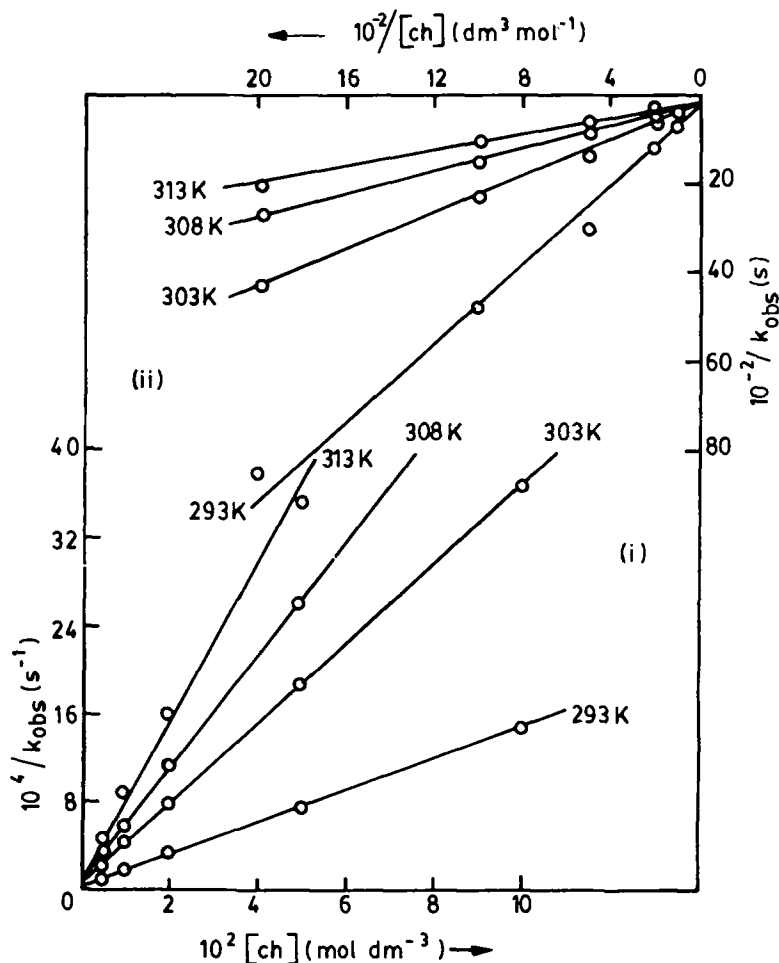
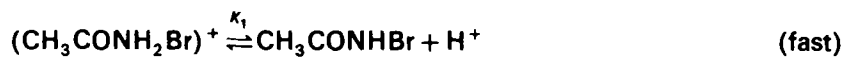


Figure 1. Plots of (a) k_{obs} versus $[\text{ch}]_0$, and (b) $1/k_{\text{obs}}$ versus $1/[\text{ch}]_0 \cdot 10^3 [\text{NBA}]_0 = 1.0 \text{ mol dm}^{-3}$, $10^3 [\text{H}^+] = 3.0 \text{ mol dm}^{-3}$ (temperature = 303 K).

in a preequilibrium step before the attack on the substrate.



where S (substrate): ch

Scheme 1.

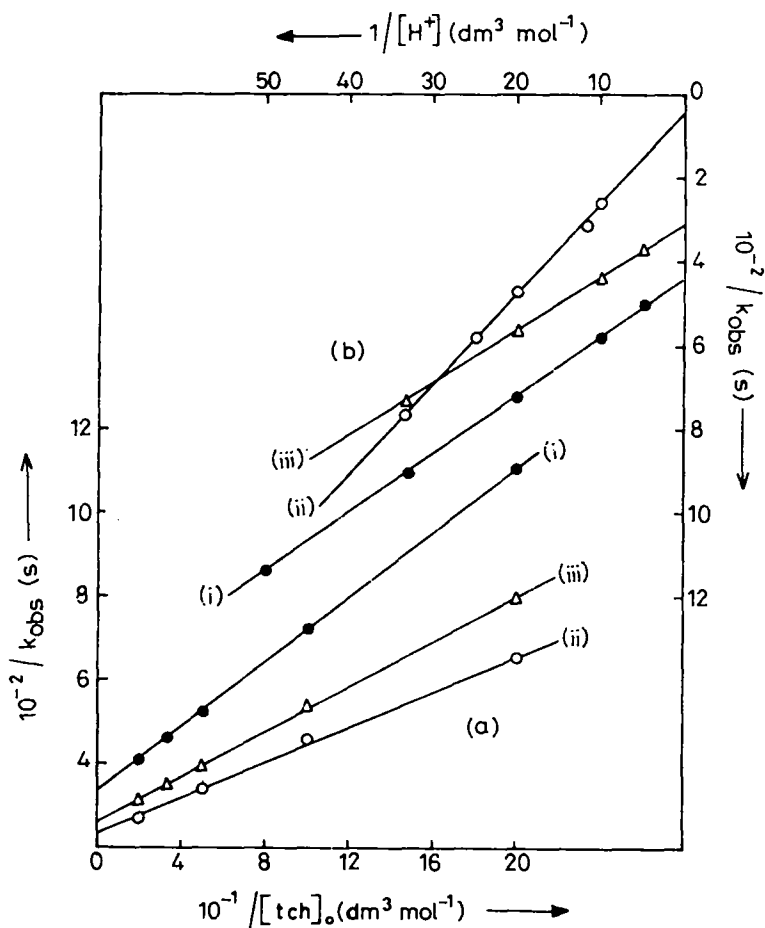


Figure 2. Plots of (a) $1/k_{\text{obs}}$ versus $1/[\text{tch}]_0$, $10^3[\text{NBA}]_0 = 1.0 \text{ mol dm}^{-3}$, $10^2[\text{H}^+] = 5.0 \text{ mol dm}^{-3}$, temperature = 283 K; and (b) $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$, $10^3[\text{NBA}]_0 = 10^2[\text{tch}]_0 = 1.0 \text{ mol dm}^{-3}$, temperature 283 K. (i) tch in the absence of KBr; (ii) tch in the presence of KBr; (iii) $\text{Zn}(\text{tch})_2\text{Cl}_2$.

Based on scheme 1, rate laws (3)–(6) have been deduced.

$$\frac{d[\text{NAB}]}{dt} = \frac{K_1 K_2 k_3 [\text{NBA}]_0 [\text{S}]}{K_1 + [\text{H}^+] + K_2 [\text{S}] [\text{H}^+] + K_1 K_2 [\text{S}]} \quad (3)$$

or

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

or

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

or

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2 [\text{S}]}{K_1 K_2 k_3 [\text{S}]} [\text{H}^+] + \frac{1 + K_2 [\text{S}]}{K_2 k_3 [\text{S}]} \quad (6)$$

Rate laws (5) and (6) predict linearities between $1/k_{\text{obs}}$ and $1/[S]$ (figure 1) and $1/k_{\text{obs}}$ and $[H^+]$ (figure not shown). The plots were linear in conformity with the predictions. The ratio of intercept to slope of the plots, $1/k_{\text{obs}}$ versus $[H^+]$ and $1/k_{\text{obs}}$ versus $1/[S]$ gave equilibrium constants K_1 and K_2 respectively: $K_1(\text{mol dm}^{-3}) = 0.0195$ and $K_2(\text{dm}^3 \text{mol}^{-1}) = 4.73$. The rate constant k_3 was calculated from the intercept of either the former plot, $k_3(\text{s}^{-1}) = 0.0101$, or the latter plot, $k_3(\text{s}^{-1}) = 0.0115$. These computed constants K_1 , K_2 and k_3 were used to predict the rate constants as $[S]$ and $[H^+]$ were varied. The comparison of predicted values with the experimental constants (table 5) shows good agreement between the two sets of values, thus indicating consistency in the rate law.

Further, the magnitudes of the four terms in the denominator of (4) are 0.0195, 0.003, 0.00014 and 0.00092. The sum of the last two terms is less than 5% of the sum of the first two terms. Hence it is not unreasonable to assume that these two terms are negligible as compared to the first two terms. With this assumption (4) takes the form

$$k_{\text{obs}} = \frac{K_1 K_2 k_3 [S]}{K_1 + [H^+]}. \quad (7)$$

Equation (7) explains the observed linearity between k_{obs} and $[ch]$ (figure 1).

If the first two steps of scheme 1 are combined then the modified scheme takes the form



Scheme 2.

The related rate laws are

$$\frac{d[\text{NBA}]}{dt} = \frac{K_4 k_5 [\text{NBA}]_0 [S]}{[H^+] + K_4 [S]} \quad (8)$$

or

$$k_{\text{obs}} = \frac{K_4 k_5 [S]}{[H^+] + K_4 [S]} \quad (9)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{[H^+]}{K_4 k_5 [S]} + \frac{1}{k_5} \quad (10)$$

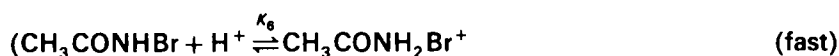
Two sets of values for constants K_4 and k_5 were calculated from the plots of $1/k_{\text{obs}}$ versus $1/[S]$ (figure 1) and $1/k_{\text{obs}}$ versus $[H^+]$ (figure not shown). The values computed from one plot were used to predict the rate constants from the rate laws for the variation of the other and vice versa. A good agreement between the predicted rate constants and experimental values (table 5) may indicate that step (i) of scheme 2 (combination of steps (i) and (ii) of scheme 1) can as well serve the purpose. But the resulting rate law cannot explain the observed linearity between k_{obs} and $[ch]$.

Further the substrate concentrations were varied at different temperatures

(293–313 K) and the constant k_5 was calculated at each temperature. The latter values were employed to calculate the activation parameters (table 4).

4.2 Oxidation of tch and its metal complex in the absence of bromide ion

Kinetics of first order in [oxidant] and fractional order in both [substrate] and $[H^+]$ may be explained by scheme 3. Here the protonated species is likely to attack the SH group of thiocarbonylhydrazide unlike in carbonylhydrazide oxidations, as the sites of attack are different in the two cases. This is evident from the observed rate dependences on $[H^+]$ for the two oxidations. It is fractional order for tch oxidation and inverse fractional order for ch oxidation.



where S (substrate): tch or its metal complex

Scheme 3.

The rate law, based on scheme 3, has been deduced as below,

$$-\frac{d[NBA]}{dt} = \frac{K_6 K_7 k_8 [NBA]_t [S][H^+]}{1 + K_6 [H^+] + K_6 K_7 [S][H^+]} \quad (11)$$

Equation (11) can be rearranged as

$$-\frac{1}{[NBA]_t} \frac{d[NBA]}{dt} = \frac{K_6 K_7 k_8 [S][H^+]}{1 + K_6 [H^+] + K_6 K_7 [S][H^+]} \quad (12)$$

If now an assumption is made that

$$-\frac{1}{[NBA]_t} \frac{d[NBA]}{dt} \approx -\frac{d \ln [NBA]}{dt} = k_{\text{obs}}$$

Then (12) takes the form

$$k_{\text{obs}} = \frac{K_6 K_7 k_8 [S][H^+]}{1 + K_6 [H^+] + K_6 K_7 [S][H^+]} \quad (13)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_6 [H^+]}{K_6 K_7 k_8 [H^+][S]} + \frac{1}{k_8} \quad (14)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_6 K_7 k_8 [S][H^+]} + \frac{1 + K_7 [S]}{K_7 k_8 [S]} \quad (15)$$

Table 6. Comparison of predicted and experimental rate constants for the oxidation of thiocarbohydrazide in the absence of added bromide ion and its metal complex by N-bromoacetamide in aqueous perchloric acid medium.

$10^4 k_{\text{obs}} (\text{s}^{-1})$				
Predicted*		Observed		
tch	Complex	tch	Complex	
$10^2 [S]_0 (\text{mol dm}^{-3})$				
0.5	9.9	12.2	9.5	11.8
1.0	14.0	18.5	13.9	17.3
2.0	18.8	24.9	18.9	23.8
3.0	21.1	28.3	21.1	28.5
5.0	23.7	31.6	25.2	33.3
$10^2 [H^+] (\text{mol dm}^{-3})$				
2.0	8.9	—	8.6	—
3.0	11.2	13.9	10.9	14.6
5.0	14.3	18.1	13.9	17.3
10.0	17.7	23.5	17.5	23.1
20.0	20.4	27.5	21.6	31.0

* Values predicted from the rate law (14) or (15) (see text)

The plots of $1/k_{\text{obs}}$ versus $1/[S]$ and $1/k_{\text{obs}}$ versus $1/[H^+]$ were linear with finite intercepts for the oxidation of both tch and its metal complex (figure 2) in accordance with the rate laws (14) and (15). Reciprocal of the former plot gave k_8 : $10^3 k_8 (\text{s}^{-1}) = 2.86$ (tch) and 3.85 (complex). The equilibrium constant K_7 was then calculated from the intercept of $1/k_{\text{obs}}$ versus $1/[H^+]$ plot by inserting k_8 and $[S]$ values ($K_7, \text{dm}^3 \text{mol}^{-1} = 500$ (tch), 650 (complex)). Further the constant K_6 was calculated from the slope of either of the two plots ($K_6, \text{dm}^3 \text{mol}^{-1} = 4.81$ (tch), 3.33 (complex)).

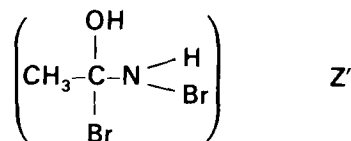
The computed constants K_6 , K_7 and k_8 were used to predict the rate constants from the rate law (13) as $[S]$ and $[H^+]$ varied. The predicted values as compared to the experimental constants are shown in table 6. Good agreement between the two sets of values provides support to the suggested mechanism.

Further, the substrate concentrations were varied at different temperatures (278–293 K) and the values for k_8 were calculated at each temperature. Activation parameters were computed from the latter constants (k_8) (table 4).

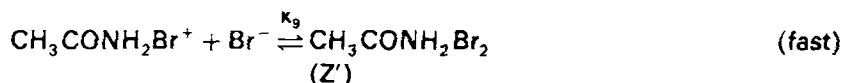
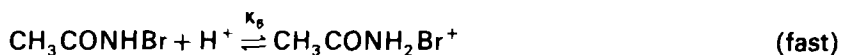
4.3 Oxidation of tch in the presence of added bromide ion

The rate showed first-order dependence on $[NBA]$ and fractional order on $[TCH]$ even under these conditions. But the rate dependence in $[H^+]$ almost doubled on the addition of bromide. These results may be explained by scheme 4. Although one may expect that the Br_2 formed from the oxidant could be the reactive species, independent reaction between Br_2 and the substrate showed that it is instantaneous. Hence if Br_2

were to be the reactive species the rate should have been independent of [substrate] contrary to present observation. Therefore an intermediate of the type proposed Z'



is quite likely rather than Br₂. The rate is also unaffected by the added reduced product of the oxidant, acetamide (table 3).



Scheme 4.

The rate of reaction is given by

$$-\frac{d[\text{NBA}]}{dt} = k_{11}[\text{Z}'']^2$$

$$= \frac{K_6 K_9 K_{10} k_{11} [\text{NBA}]_{\text{tot}} [\text{S}] [\text{H}^+] [\text{Br}^-]}{1 + K_6 [\text{H}^+] + K_6 K_9 [\text{H}^+] [\text{Br}^-] + K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}]} \quad (16)$$

or

$$k_{\text{obs}} = \frac{K_6 K_9 K_{10} k_{11} [\text{S}] [\text{H}^+] [\text{Br}^-]}{1 + K_6 [\text{H}^+] + K_6 K_9 [\text{H}^+] [\text{Br}^-] + K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}]} \quad (17)$$

$$*[\text{NBA}]_{\text{tot}} = [\text{CH}_3\text{CONHBr}] + [\text{CH}_3\text{CONH}_2\text{Br}^+] + [\text{Z}'] + [\text{Z}'']$$

$$= \frac{[\text{CH}_3\text{CONH}_2\text{Br}^+]}{K_6 [\text{H}^+]} + [\text{CH}_3\text{CONH}_2\text{Br}^+] + \text{Z}' + \text{Z}''$$

$$= \frac{1 + K_6 [\text{H}^+]}{K_6 [\text{H}^+]} \frac{\text{Z}'}{K_9 [\text{Br}^-]} + \text{Z}' + \text{Z}''$$

$$= \frac{1 + K_6 [\text{H}^+] + K_6 K_9 [\text{H}^+] [\text{Br}^-]}{K_6 K_9 [\text{H}^+] [\text{Br}^-]} \frac{\text{Z}''}{K_{10} [\text{S}]} + \text{Z}''$$

$$[\text{NBA}]_{\text{tot}} = \frac{1 + K_6 [\text{H}^+] + K_6 K_9 [\text{H}^+] [\text{Br}^-] + K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}]}{K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}]} [\text{Z}'']$$

$$[\text{Z}''] = \frac{K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}] [\text{NBA}]_{\text{tot}}}{1 + K_6 [\text{H}^+] + K_6 K_9 [\text{H}^+] [\text{Br}^-] + K_6 K_9 K_{10} [\text{H}^+] [\text{Br}^-] [\text{S}]}$$

as

$$\frac{1}{[\text{NBA}]_{\text{tot}}} \frac{d[\text{NBA}]}{dt} \approx -\frac{d \ln[\text{NBA}]}{dt} = k_{\text{obs}}$$

or

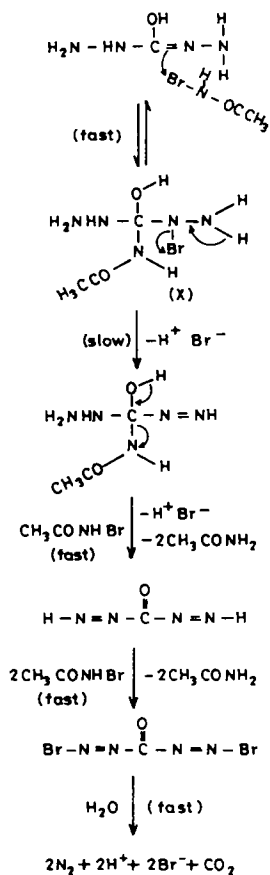
$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_6[\text{H}^+] + K_6 K_9[\text{H}^+][\text{Br}^-]}{K_6 K_9 K_{10} k_{11} [\text{H}^+][\text{Br}^-]} \frac{1}{[\text{S}]} + \frac{1}{k_{11}} \quad (18)$$

or

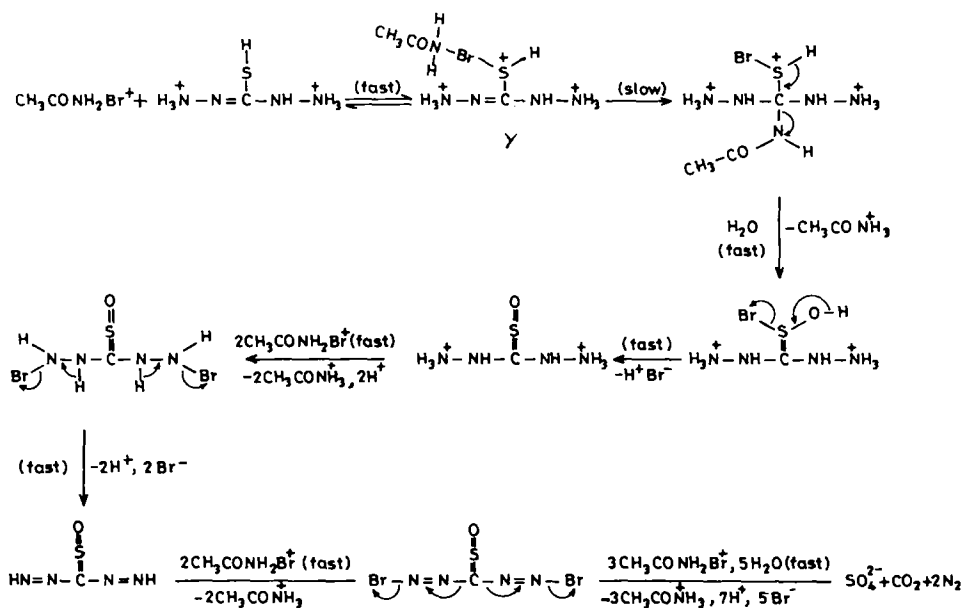
$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_6 K_9 K_{10} k_{11} [\text{Br}^-][\text{S}][\text{H}^+]} + \frac{1 + K_9[\text{Br}^-] + K_9 K_{10}[\text{S}][\text{Br}^-]}{K_9 K_{10} k_{11} [\text{S}][\text{Br}^-]} \quad (19)$$

The plots of $1/k_{\text{obs}}$ versus $1/[\text{S}]$ and $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ were linear in accordance with the rate laws (18) or (19) (figure 2).

A typical detailed mechanism of oxidation of carbohydrazide by N-bromoacetamide is shown in scheme 5, while scheme 6 gives a detailed mechanism of oxidation of thiocarbohydrazide. Under the acid conditions employed in this oxidation (0.02–



Scheme 5.



Scheme 6.

0.20 mol dm⁻³, standard-run concentration = 0.05 mol dm⁻³) it is likely that the terminal NH₂ groups get protonated. If the latter were to be the attacking points, deprotonation of -NH₃⁺ groups in the rate determining step is necessary, showing inverse dependence of rate on [H⁺], contrary to the observed fractional order dependence. Hence it is likely that the -SH group is the attacking point.

References

- Ali M A and Livingstone S E 1974 *Coord. Chem. Rev.* **13** 101 and references therein
 Burns G R 1968 *Inorg. Chem.* **7** 277
 Campbell M J M 1975 *Coord. Chem. Rev.* **15** 279, and references therein
 Duss F 1979 in *Comprehensive organic chemistry* (eds) S R Barton and W D Ollis (Oxford: Pergamon) vol. 3
 Gowda B T and Bhat J I 1987 *Tetrahedron* **43** 2119
 Gowda B T and Bhat J I 1988 *Indian J. Chem.* **A27** 597, 786, 974
 Gowda B T and Bhat J I 1989 *Indian J. Chem.* **A28** 211
 Gowda B T and Ramachandra P 1989 *J. Chem. Soc., Perkin Trans.* **2** 1067
 Gowda B T and Rao P J M 1989 *Bull. Chem. Soc. Jpn.* **62** 3303
 Gowda B T and Rao R V 1988a *Indian J. Chem.* **A27** 34
 Gowda B T and Rao R V 1988b *Oxid. Commun.* **11**, 45, 149
 Gowda B T and Rao R V 1988c *J. Chem. Soc., Perkin Trans.* **2** 355
 Gowda B T and Sherigara B S 1987 *Indian J. Chem.* **A26** 930
 Gowda B T and Sherigara B S 1989a *Int. J. Chem. Kinet.* **21** 31
 Gowda B T and Sherigara B S 1989b *Proc. Indian Acad. Sci. (Chem. Sci.)* **101** 155
 Kurzer I and Wilkinson M 1970 *Chem. Rev.* **70** 111, and references therein
 Mohr E O, Brezinski J J and Audrieth L F 1953 *Inorg. Synth.* **4** 32
 Oliveto E P and Gerold 1963 in *Organic synthesis* (ed.) H Gilmer (New York: Wiley) vol. 4, p. 104