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KINETICS AND MECHANISMS OF OXIDATION OF THIOSEMICARBAZIDE, ITS METAL COMPLEX AND HYDRAZONES BY *N*-CHLOROBENZAMIDE IN WATER METHANOL MEDIUM

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The kinetics of oxidation of thiosemicarbazide (TSC) its zinc metal complex and hydrazones by *N*-chlorobenzamide (NCB) were investigated in water methanol (1 : 1, v/v) medium in the presence of perchloric acid. The hydrazones studied were benzaldehyde, propionaldehyde, acetone and acetophenone thiosemicarbazones. The reactions show first-order kinetics in [NCB], a fractional order dependence in [substrate] and an inverse fractional to inverse first order in $[H^+]$. Addition of benzamide has no significant effect on the rates of oxidations. Variation in the ionic strength of the medium has little effect on the rates of reactions, but a decrease in the dielectric constant of the medium by increasing the methanol concentration in the solvent increases the rates. The rate-limiting steps were identified in all cases and the rate coefficients of these steps and the related activation parameters were also evaluated. The consistency of the deduced rate laws was checked by recalculating the rate constants as the substrate and H^+ concentrations were varied.

INTRODUCTION

The chemistry of hydrazine derivatives such as thiosemicarbazide and its hydrazones is of interest owing to their wide synthetic and analytical applications and biological activities.[1,2] Thiosemicarbazide ($H_2NHNCSNH_2$) is a member of the structural sequence thiourea, thiosemicarbazide and thiocarbohydrazide and has close links with thiocarbamic and thiocarbazoic acids. The chemical behaviour of thiosemicarbazide is similar to that of its keto analogue semicarbazide. Most research on thiosemicarbazides has been concentrated on the structure and bonding of their metal complexes in the solid state. Not much work has been done on the mechanistic aspects of their reactions in solution except for some work in our laboratories.[3–7] In view of the importance of this class of compounds, much work is required before rationalizing the role of these compounds in various fields of science. We report here the kinetics of oxidations of thiosemicarbazide, its metal complex and four hydrazones by *N*-chlorobenzamide in water methanol (1 : 1, v/v) medium in the presence of perchloric acid.

EXPERIMENTAL

Materials. *N*-Chlorobenzamide (NCB) was prepared by passing a continuous stream of dry chlorine into a hot saturated solution of benzamide in 1 M HCl.[8] The crystals that separated were filtered, washed with cold water and recrystallized from ethanol (m.p. 116 °C). A stock solution ($0{\cdot}10\ \text{mol dm}^{-3}$) was prepared in methanol.

Thiosemicarbazide (TSC) (Loba Chemie) was purified by recrystallization from hot water. The complex $Zn(TSC)_2SO_4$ was obtained by mixing concentrated aqueous solutions of TSC and zinc sulphate in a 2 : 1 molar ratio and scratching the sides of the container. The complex was recrystallized from hot water and characterized by recording its IR spectrum. The hydrazones benzaldehyde thiosemicarbazone (BALTSC), propionaldehyde thiosemicarbazone (PALTSC), acetone thiosemicarbazone (ACTSC) and acetophenone thiosemicarbazone (APTSC) were prepared in the laboratory by refluxing TSC and the respective aldehyde or ketone in equimolar proportions in ethanol for 2–3 h under acidic conditions. The hydrazones obtained were recrystallized from ethanol (m.p. BALTSC, 160 °C; PALTSC, 143 °C; ACTSC, 177 °C; APTSC, 113 °C). Stock solutions

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(0·05–0·10 mol dm^{-3}) of TSC in water, of the complex in 0·05 mol dm^{-3} $HClO_4$ and of the hydrazones in methanol were used. The ionic strength of the medium was maintained at 0·30 mol dm^{-3} using concentrated sodium nitrate solution.

All other reagents employed were of analytical-reagent grade.

Kinetic measurements. The reactions were carried out in glass-stoppered Pyrex boiling tubes under pseudo-first-order conditions with [substrate] ≫ [oxidant] (5–50-fold). The reactions were initiated by the rapid addition of the requisite amount of oxidant solution, thermally pre-equilibrated at a desired temperature, to solutions containing known amounts of the substrate, perchloric acid, sodium nitrate, water and methanol [to maintain a 1 : 1 (v/v) solvent composition], thermostated at the same temperature. The progress of the reactions was monitored for two half-lives by the iodimetric determination of unreacted oxidant at regular time intervals. The pseudo-first-order rate constants (k_{obs}) were reproducible to within ±4% error.

Stoichiometry and product analysis. The stoichiometries of TSC oxidant reactions in the free and metal-bound states and hydrazone oxidant reactions were determined by allowing the reactions to go to completion at room temperature and different [$HClO_4$] (0·02–0·20 mol dm^{-3}) and [substrate]/[oxidant] ratios. The products of the oxidations were identified by standard tests.[10,11] Sulphate in the reaction products was determined gravimetrically by precipitating it as barium sulphate.[12] The yields were 95 ± 4%. Chloride and cyanide were also determined by precipitating them as AgCl and AgCN, respectively. The nitrogen liberated was determined using a Schiff nitrometer. A slow and steady current of pure, dry CO_2 was passed through the reaction vessel to sweep off nitrogen to the nitrometer filled with 50% KOH, where CO_2 was completely absorbed. The volume of nitrogen was noted and compared with the theoretical value. Benzamide was almost quantitatively precipitated when the solution containing the reaction products was concentrated to remove the methanol content of the solvent and cooled.

The observed stoichiometry per mole of TSC and hydrazones may be represented by equations (1) and (2), respectively:

$$\begin{array}{c} H_2NNHCSNH_2 + 5PhCONHCl + 4H_2O \\ \downarrow \\ 5PhCONH_2 + SO_4^{2-} + 5Cl^- + N_2 + CN^- + 8H^+ \end{array} \quad (1)$$

$$\begin{array}{c} R^1R^2C{=}NHNCSNH_2 + 5PhCONHCl + 5H_2O \\ \downarrow \\ 5PhCONH_2 + SO_4^{2-} + 5Cl^- \\ + R^1R^2C{=}O + N_2 + CN^- + 8H^+ \end{array} \quad (2)$$

where R^1, R^2 = H, alkyl or aryl.

It was further observed that aldehyde or ketone does not undergo further oxidation under the present kinetic conditions.

RESULTS

The kinetics of the oxidation of thiosemicarbazide, its metal complex and hydrazones by *N*-chlorobenzamide were investigated in water methanol (1 : 1, v/v) medium in the presence of perchloric acid. The results are presented in Tables 1–3 and Figure 1. At constant [$HClO_4$], with a large excess of [substrate] (5–50-fold), the first order-plots in oxidant were linear for at least two half-lives. The pseudo-first-order rate constants calculated from the plots were unaffected by changes in

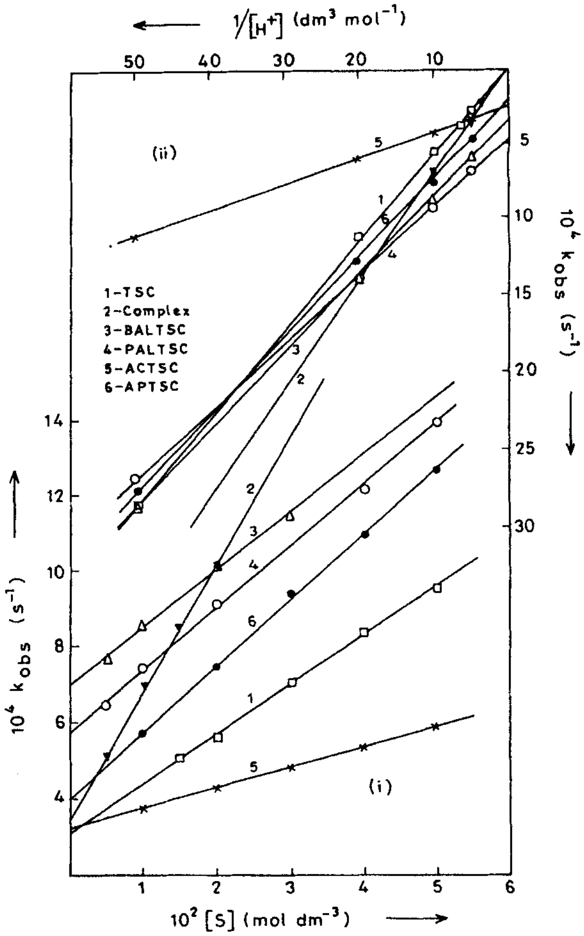


Figure 1. Plots of (i) k_{obs} vs [substrate] and (ii) k_{obs} vs $1/[H^+]$. $10^3[NCB]_0 = 1·0$ mol dm^{-3}; $I = 0·30$ mol dm^{-3}; temperature = 303 K (TSC, complex) and 293 K (hydrazones); (i) [$HClO_4$] = 0·10 mol dm^{-3}; (ii) 10^2 [substrate] (mol dm^{-3}) = 2·0 (TSC, hydrazones) and 1·0 (complex)

Table 1. Pseudo-first-order rate constants (k_{obs}) for the oxidation of thiosemicarbazide (TSC), its metal complex and hydrazones by *N*-chlorobenzamide (NCB) in water–methanol (1 : 1, v/v) medium in the presence of perchloric acid

			$10^4 k_{obs}$ (s^{-1})					
					Hydrazones[c]			
10^3 $[NCB]_0$ ($mol\,dm^{-3}$)	10^2 $[substrate]_0$[a] ($mol\,dm^{-3}$)	10^2 $[HClO_4]$ ($mol\,dm^{-3}$)	TSC[b]	Complex[b]	BALTSC	PALTSC	ACTSC	APTSC
Effect of varying $[NCB]_0$								
0·5	2·0(1·0)	10·0	5·5	6·7	8·9	9·0	4·5	7·7
1·0	2·0(1·0)	10·0	5·6	6·9	8·8	9·2	4·4	7·5
3·0	2·0(1·0)	10·0	5·6	7·0	8·8	9·2	4·3	7·4
5·0	2·0(1·0)	10·0	5·8	7·0	8·8	9·2	4·3	7·4
Effect of varying $[substrate]_0$								
1·0	0·5	10·0	—	5·1	7·7	6·5	3·0	—
1·0	1·0	10·0	4·4	7·0	8·8	7·5	3·8	5·7
1·0	1·5	10·0	5·0	8·5	—	—	—	—
1·0	2·0	10·0	5·6	10·4	10·2	9·2	4·4	7·5
1·0	3·0	10·0	7·0	—	11·5	—	5·0	9·5
1·0	4·0	10·0	8·4	—	—	12·0	5·4	11·1
1·0	5·0	10·0	9·6	—	—	14·1	6·0	12·7
Effect of varying $[HClO_4]$								
1·0	2·0(1·0)	2·0	27·0	—	28·4	26·8	11·3	27·6
1·0	2·0(1·0)	5·0	11·3	15·0	14·2	14·0	6·1	13·0
1·0	2·0(1·0)	10·0	5·6	7·0	8·8	9·2	4·4	7·5
1·0	2·0(1·0)	20·0	2·9	3·5	5·8	6·7	3·3	4·6
1·0	2·0(1·0)	30·0	—	2·3	—	—	—	—

[a] The values in parentheses are for complex and BALTSC.
[b] 303 K.
[c] 293 K.

Table 2. Effect of varying ionic strength and dielectric constant of the reaction medium on the rates of oxidation of thiosemicarbazide and its hydrazones in water–methanol (1 : 1, v/v) medium in the presence of perchloric acid

	$10^4 k_{obs}$ (s^{-1})		
		Hydrazones[b]	
I ($mol\,dm^{-3}$)	TSC[a]	BALTSC	APTSC
0.1	7.5	14.2	9.6
0.2	6.3	12.2	8.0
0.3	5.6	8.8	7.5
0.5	5.5	8.7	7.1
Methanol (%, v/v)			
30	4.0	—	—
40	4.8	7.0	5.9
50	5.6	8.8	7.5
60	6.8	11.6	8.9
70	—	13.5	10.5

[a] 303 K.
[b] 293 K.

$[NCB]_0$, establishing first-order kinetics in [NCB]. At constant $[NCB]_0$ and $[HClO_4]_0$, the rates increased with increase in [substrate] (Table 1) with varying fractional order dependences (Table 3), whereas the rates decreased with increase in $[HClO_4]$ with an inverse fractional order to inverse first-order kinetics in $[H^+]$ (Tables 1 and 3). Addition of the reduced product of the oxidant, benzamide, had no significant effect on the rate. The rates decreased slightly with increase in ionic strength of the medium, but increased with decrease in dielectric constant of the medium effected by increasing the methanol concentration in the solvent (Table 2). The rates were measured at different temperatures (288–308 K) at various [substrate] and the activation parameters were calculated from the Arrhenius and Eyring plots as described in the next section.

DISCUSSION

The probable reactive species in partial aqueous acid solutions of *N*-chlorobenzamide are PhCONHCl, $(PhCONH_2Cl)^+$ and possibly HOCl or H_2OCl^+.

The direct plots of k_{obs} versus [substrate] or k_{obs} versus $1/[H^+]$ (Figure 1) gave better correlations than

Table 3. Kinetic data and thermodynamic activation parameters for the oxidation of thiosemicarbazides by *N*-chlorobenzamide in water–methanol (1 : 1, v/v) medium in the presence of perchloric acid

Order observed in	TSC	Complex	BALTSC	PALTSC	ACTSC	APTSC
[NCB]	1·0	1·0	1·0	1·0	1·0	1·0
[Substrate]	0·58	0·60	0·25	0·35	0·28	0·51
$[H^+]$	−1·0	−1·0	−0·67	−0·62	−0·52	−0·80
Activation parameters for path 1						
E_a (kJ mol^{-1})	86·2	95·7	82·7	60·8	80·9	46·0
Log *A*	10·3	12·0	10·7	6·6	9·9	3·8
$\Delta H^{\neq}$ (kJ mol^{-1})	85·1	95·0	81·2	60·0	83·3	37·4
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−50·8	−17·2	−47·0	−121·5	−46·5	−201·8
$\Delta G^{\neq}$ (kJ mol^{-1})	100·5	100·2	95·0	95·7	97·0	96·5
Activation parameters for path 2						
E_a (kJ mol^{-1})	84·9	87·3	77·0	82·0	80·1	72·1
Log *A*	11·1	10·8	12·0	12·9	11·5	10·6
$\Delta H^{\neq}$ (kJ mol^{-1})	82·1	84·0	74·0	80·1	69·1	59·8
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−29·2	−15·1	−27·2	−4·2	−52·5	−74·3
$\Delta G^{\neq}$ (kJ mol^{-1})	90·9	88·6	82·0	81·2	84·5	81·5

the reciprocal plots (not shown). The observed kinetics and other results (Table 3) with all the hydrazones may be explained by a two-pathway mechanism, one a [substrate]-dependent path and the other a [substrate]-independent path, as detailed in Scheme 1.

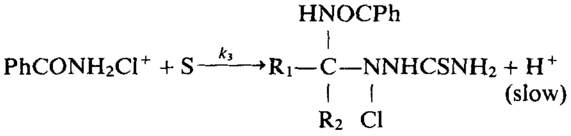
Path 1:

$$PhCONH_2Cl^+ \underset{}{\overset{K_1}{\rightleftharpoons}} PhCONHCl + H^+ \quad \text{(fast)}$$

$$PhCONHCl + H_2O \xrightarrow{k_2} PhCONH_2 + HOCl \quad \text{(slow)}$$

$$HOCl + S \longrightarrow \text{products} \quad \text{(fast)}$$

Path 2:



$$PhCONH_2Cl^+ + S \xrightarrow{k_3} R_1{-}\overset{\displaystyle HNOCPh}{\underset{\displaystyle R_2}{C}}{-}\underset{\displaystyle Cl}{N}HCSNH_2 + H^+ \quad \text{(slow)}$$

(X)

$$X + H_2O \longrightarrow S' + R_1R_2CO + PhCONH_2 \quad \text{(fast)}$$

followed by other steps similar to those in Scheme 3 where S = substrate (hydrazone)

Scheme 1

The combined rate law is

$$-\frac{d[NCB]}{dt} = \frac{K_1k_2[NCB][H_2O]}{K_1 + [^+]} + k_3[NCB][S] \qquad (3)$$

or

$$k_{obs} = \frac{K_1k_2[H_2O]}{K_1 + [H^+]} + k_3[S] \qquad (4)$$

The values of k_3 for all the hydrazones were calculated from the plots of k_{obs} versus [hydrazone] (Figure 1): 10^3k_3 (dm^3 mol^{-1} s^{-1}) = 14·8 (BALTSC), 20·7 (PALTSC), 5·3 (ACTSC) and 18·0 (APTSC).

Further, equation (4) may be rearranged to

$$\frac{1}{k_{obs} - k_3[S]} = \frac{[H^+]}{K_1k_2'} + \frac{1}{k_2'} \qquad (5)$$

where $k_2' = k_2[H_2O]$.

The plots of $1/k_{obs} - k_3[S]$ versus $[H^+]$ were linear with BALTSC and PALTSC (Figure 2). The constants k_2 and K_1 were calculated from the intercepts and slopes of the plots: 10^4k_2 dm^3 mol^{-1} s^{-1}) = 2·0 (BALTSC) and 1·5 (PALTSC); 10^3K_1 (mol dm^{-3}) = 6·8 (BALTSC) and 7·8 (PALTSC).

If $K_1 \ll [H^+]$, then equation (4) takes the form

$$k_{obs} = \frac{K_1k_2[H_2O]}{[H^+]} + k_3[S] \qquad (6)$$

or

$$k_{obs} = \frac{k}{[H^+]} + k_3[S] \qquad (7)$$

where $k = K_1k_2[H_2O]$.

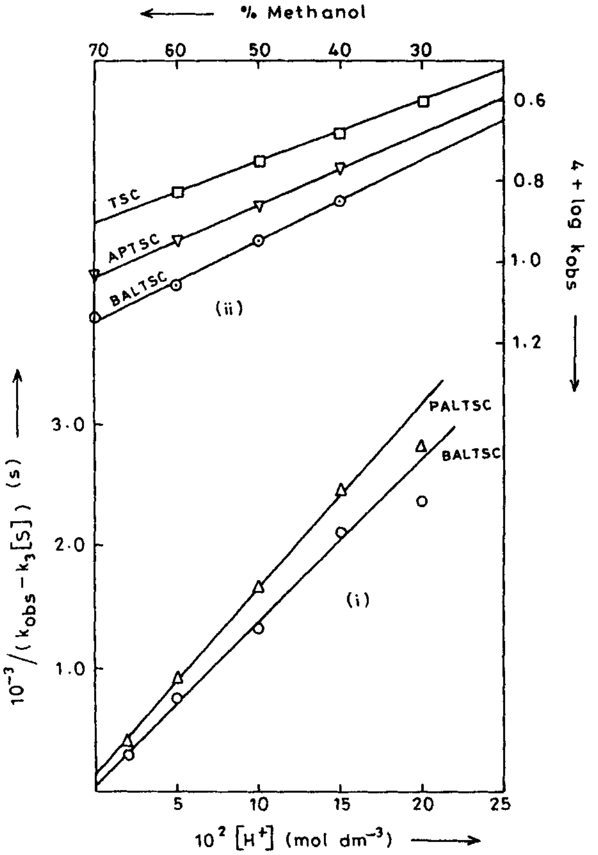


Figure 2. (i) Plot of $1/k_{obs} - k_3[S]$ vs $[H^+]$. $10^3[NCB]_0 = 1\cdot0$ mol dm^{-3}; $I = 0\cdot30$ mol dm^{-3}; 10^2 [substrate] (mol dm^{-3}) = 2·0 (hydrazones); temperature = 293 K. (ii) Plot of $\log k_{obs}$ vs methanol concentration. $10^3[NCB]_0 = 10[HClO_4] = 1\cdot0$ mol dm^{-3}; $I = 0\cdot30$ mol dm^{-3}; 10^2[substrate] = 2·0 (mol dm^{-3}) (TSC, hydrazones); temperature = 303 K (TSC) and 293 K (hydrazones)

Both plots of k_{obs} versus [S] and k_{obs} versus $1/[H^+]$ were linear in accordance with the rate law. The constants k_3 and k were calculated from the slope and intercept of the former plots and by inserting standard $[HClO_4]$ (Table 4). These constants were used to predict the rate constants from the rate law as $[HClO_4]$ was varied at constant [S]. Similarly, another set of constants, k and k_3, were calculated from the slope and intercept of k_{obs} versus $1/[H^+]$ plot and these were at constant $[HClO_4]$. There is reasonable agreement between the predicted and observed constants (Table 5). Further, the constants k and k_3 were calculated at different temperatures by varying the [substrate] at each temperature (Table 4). Two sets of activation parameters corresponding to these constants were evaluated from the plots of log(k or k_3) versus $1/T$ or $\log(k_i/T)$ versus $1/T$ (Table 3).

Oxidations of TSC and its metal complex showed an inverse first-order dependence on $[H^+]$ instead of the inverse fractional order observed with hydrazones. This is probably because the free NH_3^+ with TSC and its complex has to be deprotonated before being attacked by the oxidant. Hence the kinetics observed in these cases may be explained by a slightly modified mechanism (Scheme 2).

Path 1:

$$PhCONH_2Cl^+ \overset{K_1}{\rightleftharpoons} PhCONHCl + H^+ \quad \text{(fast)}$$

$$PhCONHCl + H_2O \xrightarrow{k_2} PhCONH_2 + HOCl \quad \text{(slow)}$$

$$HOCl + S \longrightarrow \text{products} \quad \text{(fast)}$$

Path 2:

$$SH^+ \overset{K_4}{\rightleftharpoons} S + H^+ \quad \text{(fast)}$$

$$S + PhCONH_2Cl^+ \xrightarrow{k_5} S' + PhCONH_3^+ \quad \text{(slow)}$$

followed by the other fast steps

Scheme 2

Table 4. Values of calculated constants k, k' and k_3 [see text and equations (7) and (9)] at different temperatures for the oxidation of TSC, its metal complex and hydrazones by *N*-chlorobenzamide in water–methanol (1:1, v/v) medium

Temperature (K)	10^5k (mol dm^{-3}s^{-1})						$10^4k'$ (s^{-1})		10^3k_3 (dm^{3}mol^{-1}s^{-1})			
	TSC	Complex	BALTSC	PALTSC	ACTSC	APTSC	TSC	Complex	BALTSC	PALTSC	ACTSC	APTSC
288	—	—	—	3·4	1·7	2·0	—	—	—	9·4	2·4	9·9
293	0·9	—	7·2	5·4	3·2	3·8	4·3	—	14·8	20·7	5·3	18·0
298	1·6	1·8	12·8	9·0	5·4	4·8	8·8	21·2	30·0	36·5	9·2	27·7
303	3·0	3·5	21·5	12·0	9·2	6·4	13·4	34·0	43·6	67·5	14·1	58·6
308	4·8	6·3	—	—	—	—	23·5	67·0	—	—	—	—

The related rate laws are

$$-\frac{d[\mathrm{NCB}]}{dt}=\frac{K_1k_2[\mathrm{NCB}][\mathrm{H_2O}]}{[\mathrm{H^+}]}+K_4k_5\frac{[\mathrm{NCB}][\mathrm{SH^+}]}{[\mathrm{H^+}]} \tag{8}$$

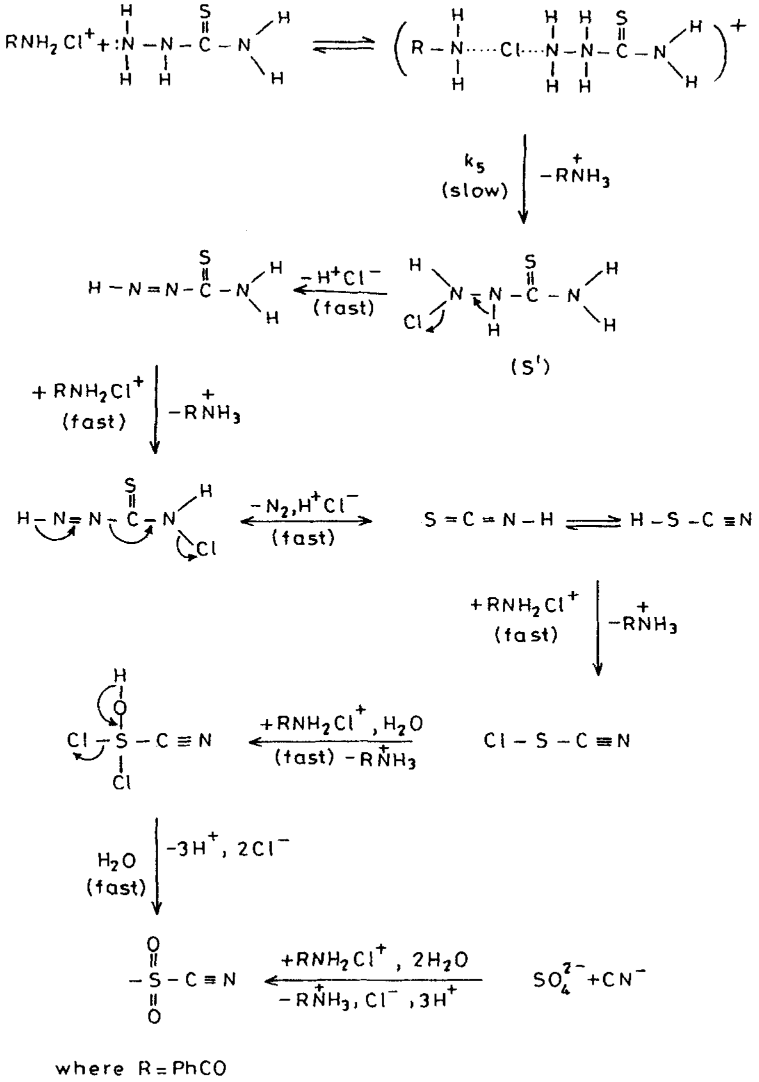
or

$$k_{\mathrm{obs}}=\frac{K_1k_2[\mathrm{H_2O}]}{[\mathrm{H^+}]}+K_4k_5\frac{[SH^+]}{[\mathrm{H^+}]}=\frac{k}{[\mathrm{H^+}]}+k'\frac{[\mathrm{SH^+}]}{[\mathrm{H^+}]} \tag{9}$$

where $k=K_1k_2[\mathrm{H_2O}]$ and $k'=K_4k_5$ or

$$k_{\mathrm{obs}}=\frac{1}{[\mathrm{H^+}]}(k+k'[\mathrm{SH^+}]) \tag{10}$$

The plots of k_{obs} versus [substrate] and k_{obs} versus $1/[\mathrm{H^+}]$ were linear with finite and no intercepts, respectively (Figure 1), in accordance with equations (9) and (10). Further, the constants k and k' (Table 4) calculated from the plots of k_{obs} versus [substrate] were used to predict the rate constants from the rate law (10) as $[\mathrm{H^+}]$ was varied (Table 6). As can be seen, there is very good agreement between the predicted values and the experimental constants, verifying the validity of the rate law.



Scheme 3

Table 5. Comparison of predicted rate constants[a] and experimental values for the oxidation of thiosemicarbazones in water–methanol (1 : 1, v/v) medium in the presence of perchloric acid

	10^4k_{obs} (s^{-1})							
	BALTSC		PALTSC		ACTSC		APTSC	
10^2 [H^+] (mol dm^{-3})	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.
2·0	36·5	28·5	31·8	26·8	17·3	11·3	23·5	27·6
5·0	15·5	14·2	14·7	14·0	7·6	6·1	11·5	13·0
10·0	8·6	8·8	9·1	9·2	4·4	4·4	7·5	7·5
20·0	5·0	5·8	6·2	6·7	2·7	3·3	5·5	4·6
10^2[S] (mol dm^{-3})								
0·5	6·8	7·7	5·6	6·5	2·4	3·0	—	—
1·0	8·6	8·8	6·8	7·5	3·1	3·8	6·0	5·7
2·0	10·2	10·2	9·1	9·2	4·4	4·4	7·5	7·5
3·0	11·7	11·5	—	—	5·6	5·0	9·0	9·5
4·0	—	—	13·7	12·0	6·9	5·4	10·2	11·2
5·0	—	—	15·8	14·1	8·2	6·0	11·6	12·7

[a] See text and equation (7).

Table 6. Comparison of predicted rate constants[a] and the experimental values for the oxidation of TSC and its metal complex by *N*-chlorobenzamide in water–methanol (1 : 1, v/v) medium.

	10^4k_{obs} (s^{-1})			
	TSC		Complex	
10^2 [H^+] (mol dm^{-3})	Pred.	Obs.	Pred.	Obs.
2·0	28·4	27·0	—	—
5·0	11·3	11·3	14·0	15·0
10·0	5·7	5·6	7·0	7·0
20·0	2·9	2·9	3·5	3·5
30·0	—	—	2·3	2·3

[a] See text and equation (10).

The reactivity of the substrates towards the oxidant decreases in the order BALTSC > PALTSC > APTSC > ACTSC ⩾ complex ⩾ TSC, indicating that the formation of hydrazone favours the reactivity of thiosemicarbazide towards the oxidant. Hydrazone formation also decreases the rate dependence on [substrate] and [H^+] (Table 3).

The typical detailed mechanism of oxidation of TSC is shown in Scheme 3.[3,4,7] The mechanism for the oxidation of hydrazones is similar to Scheme 3 except for the steps shown in path 2 in Scheme 1.

The applicability of the Taft equation[13] was also tested for both the pathways. The following relationships were found to be valid for all the hydrazones except one (Figure 3):

$$\log k_3 = -0{\cdot}27\sigma^* - 1{\cdot}07$$
$$\log k = 0{\cdot}33\sigma^* - 4{\cdot}04$$
$$\log k_3 = -0{\cdot}30E_s - 1{\cdot}02$$
$$\log k = 0{\cdot}37E_s - 4{\cdot}06$$

The negative and positive values for the polar constant (σ^*) indicate that electron-donating groups on the carbon atom of the C=N bond decrease the rate of reaction in path 1 and increase it in path 2. Similar trends were observed in steric effect plots.

The constancy of the free energies of activation may indicate the operation of similar mechanisms. The formation of more ordered activated complexes is evident from the negative values of $\Delta S^{\ddagger}$. Further, the relatively high positive free energies of activation and the negative entropy of activation may indicate the role of bond breaking in attaining the activated state. The plots of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ for both sets of values (Table 3) were linear with isokinetic temperatures of 336 and 315 K, respectively.

Several approaches have been put forward to explain quantitatively the effect of the dielectric constant of the medium on the rates of ion–ion, ion–dipolar molecule and dipolar molecule–dipolar molecule reactions in the liquid phase.[14–17] For the limiting case of a zero angle of approach between an ion and a dipole, Amis[14] has shown that a plot of log k_D versus $1/D$ gives a straight line with a positive slope for the reaction between a positive ion and a dipolar molecule:

$$\log k_D = \log k_\infty + \frac{Ze\mu}{2{\cdot}303k_bTr^2D}$$

where k_∞ is the rate constant in a medium of infinite dielectric constant D, μ is the dipole moment of the dipolar molecule, Ze is the charge on the ion, r the radius and T the absolute temperature. The present experimental observations, i.e. an increase in rate with a decrease in dielectric constant of the medium (by increasing the methanol composition of the medium from 30 to 70%, v/v) is in agreement with ion–dipolar molecule interactions and the reaction pathways suggested to explain the kinetic results. The observed

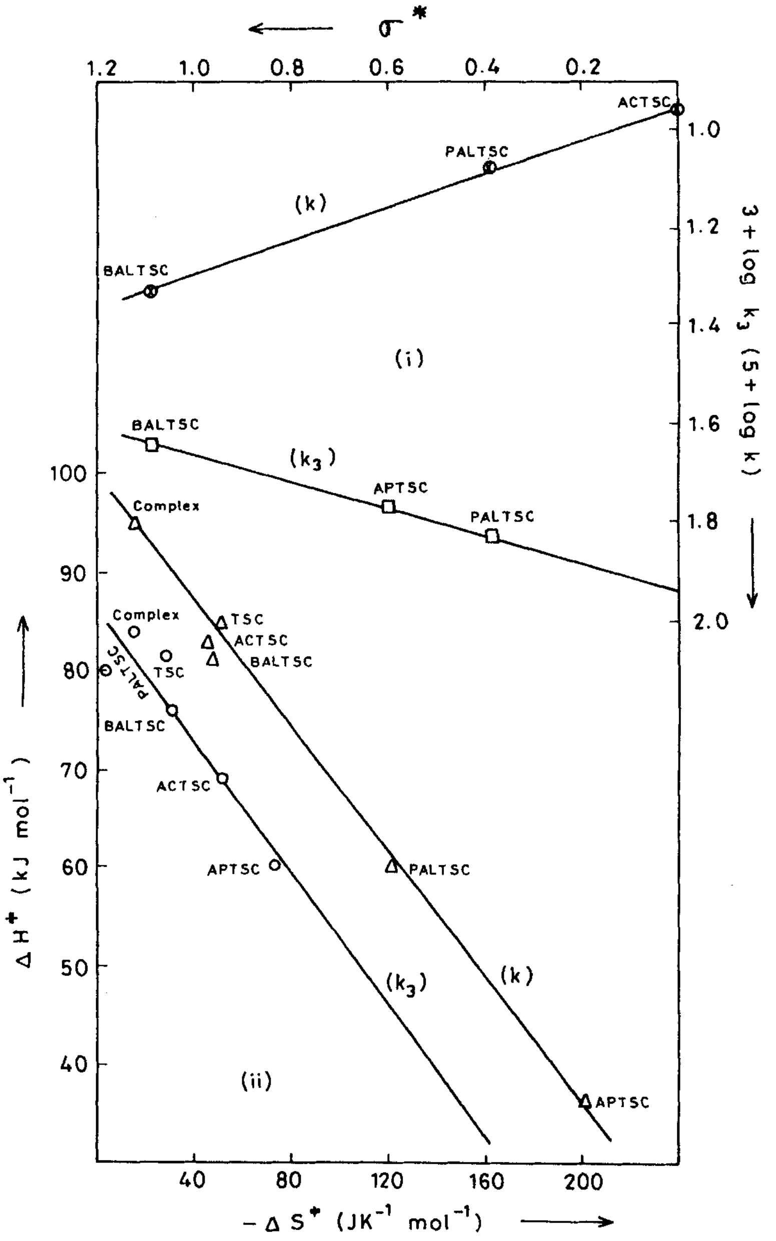


Figure 3. (i) Plots of log k_3 vs σ^* and log k vs σ^*; (ii) plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$

effect may also be explained by the Laidler–Eyring equation:[17]

$$\log k_{\mathrm{D}} = \log k + \frac{Z^2 e^2}{2 D k_{\mathrm{b}} T} \left(\frac{1}{r} - \frac{1}{r_{\ddagger}} \right)$$

where r and $r_{\ddagger}$ refer to the radius of the reactant species and activated complex, respectively. It is seen that the rate should be greater in a medium of lower dielectric constant when $r_{\ddagger} > r$. It is likely that the radii of the activated complexes in the present cases are greater than the reactant molecules, as the reaction involves the interaction between positive ions and dipolar molecules.

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REFERENCES

1. F. Duus, in *Comprehensive Organic Chemistry*, edited by S. R. Barton and W. D. Ollis, Vol. 3, p. 452. Pergamon Press, Oxford (1979).
2. M. J. M. Campbell, *Coord. Chem. Rev.* **15**, 279 (1975), and references cited therein.
3. B. T. Gowda and B. S. Sherigara, *Int. J. Chem. Kinet.* **21**, 31 (1989).
4. B. T. Gowda and P. Ramachandra, *J. Chem. Soc., Perkin Trans. 2* 1067 (1989); *Indian J. Chem.* **29A**, 680 (1990); *Proc Indian Acad. Sci. (Chem. Sci.)* **102**, 471 (1990).
5. B. T. Gowda, V. Pardhasaradhi and P. Ramachandra, *Indian J. Chem.* **29A**, 1192 (1990); *Oxid. Commun.* **14**, 163 (1991).
6. B. T. Gowda and P. S. K. Kumar, *Z. Phys. Chem., N. F.* **167**, 151 (1990).
7. B. T. Gowda and P. J. M. Rao, *Z. Phys. Chem., N. F.* **168**, 183 (1990); *Proc. Indian Acad. Sci. (Chem. Sci.)* **103**, 55 (1991); *Indian J. Chem.* **30A**, 148 (1991).
8. B. S. Rawat and M. C. Agrawal, *Indian J. Chem.* **15A**, 713 (1977).
9. B. A. Gingras, R. W. Hornal and C. H. Bayley, *Can. J. Chem.* **38**, 712 (1960).
10. G. Svehla, *Vogel's Text Book of Macro and Semimicro Qualitative Inorganic Analysis*. Longman, London (1982).
11. B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, *Vogel's Text Book of Practical Organic Chemistry*. Longman, London (1984).
12. J. Bassett, R. C. Denney, G. H. Jeffery and J. Mendham, *Vogel's Text Book of Quantitative Inorganic Analysis*. Longman, London (1978).
13. R. W. Taft, Jr, in *Steric Effects in Organic Chemistry*, edited by M. Newman. Wiley, New York (1956).
14. E. S. Amis, *Solvent Effects on Reaction Rates and Mechanisms*. Academic Press, New York (1966).
15. S. G. Entelis and R. P. Tiger, *Reaction Kinetics in the Liquid Phase*. Wiley, New York (1976).
16. P. Zuman and R. C. Patel, *Techniques in Organic Reaction Kinetics*. Wiley, New York (1984).
17. K. J. Laidler and H. Eyring, *Ann. N.Y. Acad. Sci.* **39**, 303 (1940).