

Kinetics of oxidation of S–N donor ligands by hydrogen peroxide

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Abstract. The kinetics of oxidation of thiosemicarbazide (TSC) in aqueous perchloric and sulphuric acid media, and also that of thiocarbohydrazide (TCH), its metal complex and its hydrazone in perchloric acid medium, by hydrogen peroxide have been investigated under varying conditions. The rates show first order kinetics each in [oxidant] and [substrate] in all the cases. The rate dependences in $[H^+]$ are different. Inverse first order kinetics in $[H^+]$ are observed for TCH oxidations and varying inverse orders in $[H^+]$ (depending upon its concentration) are seen for TSC oxidations. Effects of varying ionic strength, dielectric constant of the medium etc. have also been investigated. Mechanisms consistent with the observed results have been considered and discussed. The metal complexation of thiocarbohydrazide and its conversion into hydrazone enhance the rate of oxidations but have little effects on the kinetic orders.

Keywords. Kinetics of oxidation; thiosemicarbazide; thiocarbohydrazide; hydrogen peroxide; acid medium.

1. Introduction

The chemistry of S–N donor ligands such as thiosemicarbazide, thiocarbohydrazide and their homologues has evoked keen interest owing to their biological activities and wide synthetic and analytical applications (Kurzer and Wilkinson 1970; Ali and Livingstone 1974; Campbell 1975). Most of the research on these compounds is centred on the structure and bonding of their metal complexes in the solid state. Very little is known of their reactions in solution. In an effort to provide some insights into the mechanism of their activities in solution, we have initiated some work on these compounds (Gowda and Bhat 1987–1989; Gowda and Sherigara 1987, 1989; Gowda and Rao 1988, 1989; Gowda and Ramachandra 1989). As a part of these efforts, the kinetics of oxidation of thiosemicarbazide and thiocarbohydrazide, and the metal complex and the hydrazone of the latter compound, by hydrogen peroxide have been studied in aqueous perchloric and sulphuric acid media under varying conditions.

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2. Materials and methods

Analytical grade H_2O_2 was used and its aqueous solution standardised just before use. Thiosemicarbazide (TSC) (E Merck) was purified by recrystallisation from hot water. An aqueous stock solution (0.10 mol dm^{-3}) of the compound was used.

Thiocarbohydrazide (TCH) was prepared by refluxing the mixture of carbon disulphide and hydrazine hydrate at 90° for a period of 1h (Burns 1968). The complex, $\text{Zn}(\text{TCH})_2\text{Cl}_2$ was obtained by mixing warm solutions of ZnCl_2 in dimethyl formamide (DMF)–water (5:1, v/v) and TCH in DMF in 1:2 mole ratio (Burns 1968). The thiocarbohydrazone, *bis*-ethylidene thiocarbohydrazide was prepared by refluxing a mixture of acetaldehyde in ethanol and TCH in 1 mol dm^{-3} acetic acid for one hour (Guha and De 1935).

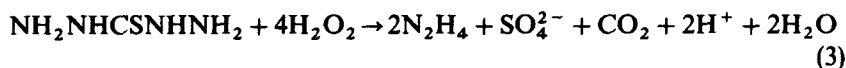
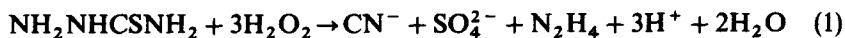
The stock solutions (0.05 mol dm^{-3}) of TCH, its metal complex and its hydrazone were prepared in 0.10 mol dm^{-3} aqueous perchloric acid, as their aqueous solutions were unstable and decomposed on standing. Preliminary investigations showed that variation in ionic strength of the medium has no significant effect on the rates of all the reactions. All other reagents used were of accepted grades of purity.

2.1 Kinetic measurements

The kinetic studies were carried out under pseudo-first order conditions with $[\text{substrate}] \gg [\text{oxidant}]$ (5 to 80-fold excess). The reactions were initiated by the rapid addition of requisite amounts of oxidant solution, thermally pre-equilibrated at a desired temperature, to solutions containing known amounts of the substrate ($0.005\text{--}0.05 \text{ mol dm}^{-3}$), acid ($0.001\text{--}0.10 \text{ mol dm}^{-3}$) and water, thermostatted at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric estimation 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 $\pm 3\%$.

2.2 Stoichiometry and product analysis

Stoichiometries of the substrate–oxidant reactions were determined at different temperatures (293–313 K) under varying $[\text{HClO}_4]$ ($0.001\text{--}0.10 \text{ mol dm}^{-3}$) and under excess oxidant conditions. TSC and TCH (or its metal complex or hydrazone) are oxidised to the sulphate to the extent of about 65 and 40%, respectively, in all the cases. The other products are the corresponding keto compounds and sulphur. The observed stoichiometries may be represented as below.



The semicarbazide formed was quantitatively determined by oxidising it with acid bromate and determining the volume of liberated nitrogen. With thiocarbohydrazide, a coloured compound separated out on increasing the concentrations of the reactants.

3. Results

The kinetics of oxidation of TSC in aqueous perchloric and sulphuric acid media, TCH and its metal complex and hydrazone in aqueous $HClO_4$ by H_2O_2 have been studied under varying conditions. The results are shown in tables 1–3.

3.1 Oxidation of thiosemicarbazide

At fixed [acid] and with several-fold excess of [TSC], the plots of $\log [H_2O_2]_0/[H_2O_2]$ versus time were linear for at least two half-lives. The pseudo-first-order rate constants (k_{obs}) computed from the plots were almost unaffected by the changes in $[H_2O_2]_0$ in both perchloric and sulphuric acid media. The rates decreased with increase in $[H^+]$ in both the acid media, but the effect was more pronounced at $[H^+] > 0.01 \text{ mol dm}^{-3}$. In sulphuric acid media, $[SO_4^{2-}]$ was kept constant while varying $[H_2SO_4]$. [TSC] and $[H_2O_2]$ were varied in both the media in the two ranges of [acid] (table 1). The rates increased with increase in [TSC] with almost first-order kinetics in [TSC]. The rates slightly decreased with increase in $[H_2O_2]$ in $HClO_4$ medium, while they remained almost constant in H_2SO_4 medium (table 1). Variations in either the ionic strength or dielectric constant (by changing solvent composition with methanol) of

Table 1. Pseudo-first order rate constants (k_{obs}) for the oxidation of thiosemicarbazide (TSC) by hydrogen peroxide in aqueous perchloric and sulphuric acid media at 303 K.

$10^3[H_2O_2]_0$ (mol dm^{-3})	$10^2[TSC]_0$ (mol dm^{-3})	$10^2[\text{Acid}]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	$10^3[H_2O_2]_0$ (mol dm^{-3})	$10^2[TSC]_0$ (mol dm^{-3})	$10^2[\text{Acid}]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
<i>Perchloric acid medium</i>							
0.5	2.0	0.5	8.9	0.5	4.0	5.0	6.6
1.0	2.0	0.5	8.8	1.0	4.0	5.0	6.4
2.0	2.0	0.5	8.4	2.0	4.0	5.0	6.2
4.0	2.0	0.5	8.0	5.0	4.0	5.0	5.8
1.0	0.5	0.5	1.7	1.0	0.5	5.0	0.77
1.0	1.0	0.5	3.8	1.0	1.0	5.0	1.34
1.0	3.0	0.5	12.9	1.0	2.0	5.0	3.12
1.0	5.0	0.5	21.9	1.0	5.0	5.0	8.90
1.0	2.0	0.1	11.8	1.0	4.0	2.0	11.8
1.0	2.0	0.2	10.3	1.0	4.0	3.0	9.3
1.0	2.0	1.0	8.2	1.0	4.0	10.0	3.9
<i>Sulphuric acid medium</i>							
0.5	2.0	1.0	7.9	0.5	5.0	7.0	5.6
1.0	2.0	1.0	7.4	1.0	5.0	7.0	5.6
2.0	2.0	1.0	7.3	2.0	5.0	7.0	5.5
4.0	2.0	1.0	7.3	5.0	5.0	7.0	5.3
1.0	0.5	1.0	2.0	1.0	0.7	7.0	0.74
1.0	1.0	1.0	4.0	1.0	2.0	7.0	2.31
1.0	3.0	1.0	10.8	1.0	3.0	7.0	3.5
1.0	5.0	1.0	19.3	1.0	7.0	7.0	7.2
1.0	2.0	0.5	9.4	1.0	5.0	5.0	7.4
1.0	2.0	2.0	5.2	1.0	5.0	10.0	3.6
1.0	2.0	3.0	4.8	1.0	5.0	15.0	2.5
1.0	2.0	5.0	3.6				

Table 2. Pseudo-first order rate constants for the oxidation of thiocarbohydrazide (TCH), its metal complex and its hydrazone, by hydrogen peroxide in aqueous perchloric acid medium at 303 K.

$10^3[\text{H}_2\text{O}_2]_0$ (mol dm ⁻³)	$10^2[\text{substrate}]_0^a$ (mol dm ⁻³)	$10^2[\text{HClO}_4]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}(\text{s}^{-1})$		
			TCH	Complex	Hydrazone
0.5	2.0(1.0)	3.0	2.83	2.29	2.80
1.0	2.0(1.0)	3.0	2.97	2.34	2.85
2.0	2.0(1.0)	3.0	2.98	2.36	2.93
4.0	2.0(1.0)	3.0	—	2.39	2.95
5.0	2.0(1.0)	3.0	2.99	—	—
1.0	0.3	3.0	—	0.64	—
1.0	0.5	3.0	0.79	1.13	1.42
1.0	1.0	3.0	1.51	2.34	2.85
1.0	2.0	3.0	2.97	4.30	6.14
1.0	4.0	3.0	6.01	—	—
1.0	2.0(1.0)	2.0	4.36	3.09	4.16
1.0	2.0(1.0)	3.0	2.97	2.34	2.85
1.0	2.0(1.0)	5.0	1.58	1.20	1.62
1.0	2.0(1.0)	10.0	0.99	0.63	—

^a Values in parentheses are [complex] and [hydrazone].

Table 3. Kinetic data and activation parameters for the oxidation of thiosemicarbazide (TSC) and thiocarbohydrazide (TCH), its metal complex and its hydrazone, by H₂O₂ in acid medium.

Order (<i>n</i>) observed in	Thiosemicarbazide				Thiocarbohydrazide		
	[HClO ₄](mol dm ⁻³)		[H ₂ SO ₄](mol dm ⁻³)		TCH	Complex	Hydrazone
	0.001–0.01	0.02–0.1	0.005–0.05	0.05–0.15			
[H ₂ O ₂]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[substrate]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[H ⁺]	-0.16	-0.78	-0.45	-1.13	-1.0	-1.0	-1.0
<i>Activation parameters</i>							
<i>E_a</i> (kJ mol ⁻¹)	54.2	76.6	68.1	89.6	45.0	52.1	52.6
Log <i>A</i>	6.28	10.0	8.61	12.2	4.23	5.35	5.53
ΔH^\ddagger (kJ mol ⁻¹)	51.1	73.1	67.2	90.1	42.4	49.0	49.2
ΔS^\ddagger (JK ⁻¹)	-135.1	-64.9	-83.2	-10.0	-172.7	-153.0	-150.5
ΔG^\ddagger (kJ mol ⁻¹)	92.0	92.8	92.4	93.1	94.7	95.3	94.8

the medium had no significant effect on the rates of oxidations in all the cases (values not shown).

3.2 Oxidation of thiocarbohydrazide, its metal complex and hydrazone

The first-order plots were linear at least for two half-lives for all the oxidations. Further, the pseudo-first order rate constants (k_{obs}) computed from the plots were insensitive to the variations in [H₂O₂], at constant [substrate] and [HClO₄] (table 2). At fixed

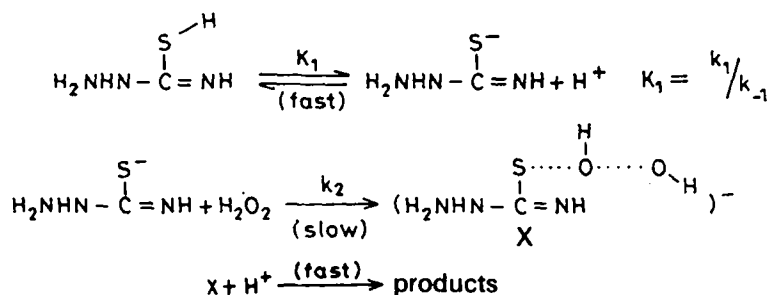
[H₂O₂] and [HClO₄], the rates increased with increase in [substrate] with first order dependences (tables 2 and 3). The rates decreased with increase in [HClO₄] with an inverse first-order dependence in [H⁺]. But the rates were unaffected by variations in either ionic strength or solvent composition (with methanol) of the medium.

The rates were measured at different temperatures and the activation parameters computed in all the cases (table 3).

4. Discussion - mechanisms of oxidations

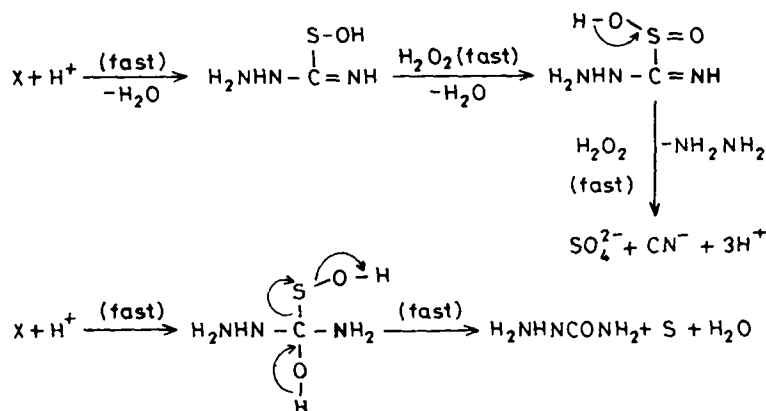
4.1 Oxidation of thiosemicarbazide

The observed kinetics (table 3) may be explained by a mechanism shown in scheme 1.



Scheme 1.

The common intermediate X undergoes branching reactions (disproportionation and/or further reactions with H₂O₂) to give different products. In one of the paths it leads to sulphate and in the other it gives the OXO-product.



Scheme 2.

Sulphate was determined at different temperatures (293–313 K) under varying [acid] (0.001–0.10 mol dm⁻³). TSC gets oxidised to sulphate to the extent of about 65% under all conditions. The OXO-product was also quantitatively determined as described under stoichiometry and product analysis.

The rate law (4) in accordance with scheme 1 has been deduced as

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{K_1 k_2 [\text{S}]_0 [\text{H}_2\text{O}_2]}{K_1 + [\text{H}^+] + (k_2/k_{-1})[\text{H}_2\text{O}_2]}, \text{ where } [\text{S}] = [\text{S}]_0 - [\text{S}^-]. \quad (4)$$

Equation (4) may be rearranged as

$$\begin{aligned} -\frac{1}{[\text{H}_2\text{O}_2]} \frac{d[\text{H}_2\text{O}_2]}{dt} &= -\frac{d \ln [\text{H}_2\text{O}_2]}{dt} = k_{\text{obs}} \\ &= \frac{K_1 k_2 [\text{S}]_0}{K_1 + [\text{H}^+] + (k_2/k_{-1})[\text{H}_2\text{O}_2]}. \end{aligned} \quad (5)$$

Since $(K_1 + [\text{H}^+]) \gg (k_2/k_{-1})[\text{H}_2\text{O}_2]$ rate law (5) reduces to

$$k_{\text{obs}} = \frac{K_1 k_2 [\text{S}]_0}{K_1 + [\text{H}^+]}. \quad (6)$$

The plot of k_{obs} versus $[\text{TSC}]$ was linear in accordance with rate law (6). Rate law (5) also accounts for slight decrease of rate with increase in $[\text{H}_2\text{O}_2]$ (table 1).

With $[\text{H}^+] > 0.01 \text{ mol dm}^{-3}$, K_1 will be very small as the equilibrium lies towards the left and hence the rate law further reduces to

$$k_{\text{obs}} = \frac{K_1 k_2 [\text{S}]_0}{[\text{H}^+]}. \quad (7)$$

The rate law (7) explains the observed nearly inverse first order in $[\text{H}^+]$ and the plots are linear in accordance with the rate law.

4.2 Oxidation of thiocarbohydrazide, its metal complex and hydrazone

Kinetics of these oxidations were studied at $[\text{H}^+] > 0.01 \text{ mol dm}^{-3}$. The results observed under these conditions (table 3) may be explained by a mechanism similar to scheme 1 and the related rate law (7). The plots of k_{obs} versus $[\text{substrate}]$ and k_{obs} versus $1/[\text{H}^+]$ gave straight lines passing through the origin.

The metal complexation of TCH and its conversion into hydrazone enhanced the rate of oxidations but had little effect on the kinetic orders. Change in the acid medium from HClO_4 to H_2SO_4 had also negligible effect on the kinetics of oxidation. The constancy of free energies of activation (table 3) shows that similar mechanisms are operative in all the cases. Relatively high positive values of ΔG^\ddagger may signal bond breaking in the formation of transition states. Large ΔS^\ddagger values indicate that the transition states are more ordered than reactants due to decrease in the number of degrees of freedom (Zuman and Patel 1984; Laidler 1987).

References

- Ali M A and Livingstone S E 1974 *Coord. Chem. Rev.* **13** 101
 Burns G R 1968 *Inorg. Chem.* **7** 277
 Campbell M J M 1975 *Coord. Chem. Rev.* **15** 279

- 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 *Oxidn. 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
Guha P C and De S C 1935 *J. Indian Chem. Soc.* **12** 225
Kurzer I and Wilkinson M 1970 *Chem. Rev.* **70** 111
Laidler K J 1987 *Chemical kinetics* (New York: Harper and Row)
Zuman P and Patel R C 1984 *Techniques in organic reaction kinetics* (New York: Wiley)