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Kinetics of Oxidation of Thiocyanate and Thiosemicarbazide in the Free and Metal-bound States by Potassium Iodate in Aqueous Perchloric Acid Medium

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Kinetics of oxidation of thiocyanate ion and thiosemicarbazide (TSC) in the free and metal-bound states by potassium iodate have been studied in aqueous perchloric acid medium under varying conditions. Oxidation of thiocyanate showed first order kinetics in $[KIO_3]$ and nearly first order in $[NCS^-]$. The rate was independent of $[H^+]$. Variation in either the ionic strength or dielectric constant of the medium had no effect on the rate of reaction Oxidation of thiosemicarbazide in the free and metal-bound states showed first order kinetics in $[KIO_3]$, a little fractional order in [TSC] and inverse fractional order in $[H^+]$. Variation in ionic strength of the medium and addition of iodide to reaction mixture slightly decreased the rate. Variation in dielectric constant of the medium by changing the solvent composition with methanol had no significant effect on the rate. Mechanisms consistent with the observed results have been considered and discussed. Activation parameters have also been calculated by measuring rates at different temperatures. The metal complexation of the ligand makes the rate independent of its concentration.

THE chemistry of S–N donor ligands such as thiosemicarbazide and their homologues has evinced keen interest due to their biological activities and wide synthetic and analytical applications. Most of the chemical research with these compounds is centred on structure and bonding of their metal complexes in the solid state[1-3]. Very little is known about the mechanisms of their reactions in solution. Recently some work in this direction has been initiated in our laboratories[4]. The main object is to provide an insight into the mechanisms of their activities in solution. Thiocyanates also find a number of industrial applications and as reagents in analytical chemistry.

We report herein the kinetics and mechanism of oxidation of thiocyanate and thiosemicarbazide in the free and Zn^{II}-bound states by potassium iodate in aqueous perchloric acid medium.

Experimental

The purity of potassium iodate (A.R., E. Merck) was checked by iodometric method, in its aqueous stock solution (0.01 mol dm^{-3}). Potassium thiocyanate (A.R.) aqueous solution ($\sim$0.5 mol dm^{-3}) was standardised by argentometric method[5]. Thiosemicarbazide (TSC) (E. Merck) was purified by recrystallisation and its aqueous stock solution (0.10 mol dm^{-3}) was prepared. The Zn^{II} complex of TSC was prepared by mixing aqueous solution of TSC and $ZnSO_4$ in 2 : 1 ratio and scratching the sides of the container. The sample was recrystallised from water and characterised by its ir spectra, elemental analysis and by analytical estimations[3]. A stock solution (0.02 mol dm^{-3}) of the complex in $HClO_4$ (0.03 mol dm^{-3}) was prepared. The ionic strength of the reaction medium was kept at 0.50 mol dm^{-3} (0.3 mol dm^{-3} in TSC complex oxidation) using concentrated aqueous solution of sodium perchlorate. All other reagents were of accepted grades of purity.

Stoichiometry : The stoichiometries of KIO_3-NCS^- and KIO_3-TSC (in the free and Zn^{II}-bound states) reactions were determined by allowing the reactions to go to completion at different [substrate] to $[KIO_3]$ ratios and $[H^+]$ (0.01–0.20 mol dm^{-3}) in aqueous solutions at 303 K. The products sulphate and cyanide in the reaction mixtures were detected by standard tests[6]. Further, sulphate was estimated gravimetrically[5]. The yields were 98 ± 5%. The observed stoichiometries may be represented by equations (1) and (2).

$$KCNS+KIO_3+H_2O \rightarrow KI+SO_4^{2-}+KCN+2H^+ \tag{1}$$

$$3NH_2NHCSNH_2+5KIO_3 \rightarrow 3SO_4^{2-}+3N_2+3CN^- +5KI+3H_2O+9H^+ \tag{2}$$

Results and Discussion

The results of these study are shown in Tables 1–4 and Figs. 1 and 2.

Oxidation of thiocyanate ion : At fixed $[NCS^-]$ (several fold excess over the $[KIO_3]$) and $[H^+]$, the plots of log $[KIO_3]_0/[KIO_3]$ vs time were linear for at least two half-lives. The pseudo-first order rate constants (k_{obs}) calculated from the plots were insensitive to the variations in $[KIO_3]_0$ (Table 1), establishing first order kinetics in [KIO_3]. The rate increased with increase in [NCS^-] with almost first order dependence at constant [KIO_3] and [H^+]. The rate was almost independent of [H^+] (Table 1). Addition of potassium iodide slightly decreased the rate. But the variation in ionic strength or dielectric constant of medium by changing the solvent composition with methanol had no effect on the rate of oxidation.

Oxidation of TSC in the free and Zn^{II}-bound states : The plots of log [oxidant] vs time were linear for at least two half-lives. Pseudo-first order rate constants (k_{obs}) computed from the first order plots were insensitive to the variation in [oxidant] for oxidation of TSC both in the free and Zn^{II}-bound states (Tables 2 and 3). At fixed [oxidant] and [$HClO_4$], the rate increased with increase in [TSC] with a little fractional order in [TSC]. The rate was independent of [complex]. The rates decreased with increase in [$HClO_4$] for both the oxidations with fractional order dependences in [H^+] (Tables 2–4).

Variation in ionic strength of the medium or addition of potassium iodide had little effect on the rate. The variation in dielectric constant of the medium by changing the solvent composition with methanol had no significant effect on the rates.

The [substrate] were varied at different temperatures (in case where the substrate dependence was observed) and the constants of the rate-limiting steps

TABLE 1—PSEUDO-FIRST ORDER RATE CONSTANTS (k_{obs}) FOR OXIDATION OF THIOCYANATE BY POTASSIUM IODATE*

$[KIO_3]_0$ $\times 10^3$ mol dm^{-3}	$[NCS^-]_0$ $\times 10^2$ mol dm_{-3}	$[HClO_4]$ $\times 10^2$ mol dm^{-3}	k_{obs} $\times 10^4$ s^{-1}	μ mol dm^{-3}	k_{obs} 10^4 s^{-1}
0.3	2.0	5.0	5.6	0.07	5.7
0.5	2.0	5.0	5.7	0 2	5 6
1.0	2.0	5.0	5.6	0.5	5.6
1.5	2.0	5.0	5.6	1.0	5.7
2.0	2.0	5.0	5.7	%Methanol	
1.0	0.5	5 0	1.5	0.0	5.6
1.0	1.0	5.0	2.9	5.0	5.7
1.0	2.0	5.0	5.6	10.0	5.7
1.0	5.0	5.0	11.8	20.0	5.6
1.0	10.0	5.0	22.1	40.0	5.7
1.0	2.0	1.0	5.7	[KI] ($\times 10^3$ mol dm^{-3})	
1.0	2.0	2.0	5 6		
1.0	2.0	5.0	5.6	0.0	5.6
1.0	2.0	10.0	5.4	1.0	3.5
1.0	2.0	20.0	5.3	10.0	1.9

*10^3 $[KIO_3]_0$=1 0 mol dm^{-3} ; 10^2 $[NCS^-]_0$=2.0 mol dm^{-3} ; 10^2 $[HClO_4]$=5.0 mol dm^{-3} ; μ=0.50 mol dm^{-3} (except during its variation) ; Temp.=298 K.

TABLE 2—PSEUDO-FIRST ORDER RATE CONSTANTS (k_{obs}) FOR OXIDATION OF THIOSEMICARBAZIDE (TSC) BY POTASSIUM IODATE*

$[KIO_3]_0$ $\times 10^2$ mol dm^{-3}	$[TSC]_0$ $\times 10^3$ mol dm^{-3}	$[HClO_4]$ $\times 10$ mol dm^{-3}	k_{obs} $\times 10^4$ s^{-1}	μ mol dm^{-3}	k_{obs} $\times 10^4$ s^{-1}
0.2	2.0	1.0	3.0	0.121	5.2
0.5	2.0	1.0	3.0	0.2	3.9
1.0	2.0	1.0	3.1	0.5	3.1
2.0	2.0	1.0	3.1	1.0	2.7
4.0	2.0	1.0	3.0	% Methanol	
1.0	0.5	1.0	2.6	0	3.1
1.0	1.0	1.0	2.9	5	3.4
1.0	2.0	1.0	3.1	10	3.5
1.0	4.0	1.0	3.3	20	3.5
1.0	6.0	1.0	3.5	40	3.6
1.0	2.0	0.1	14.1	[KI] ($\times 10$ mol dm^{-3})	
1.0	2.0	0.2	9.3	0	3.1
1.0	2.0	0.5	4 6	5	3.4
1.0	2.0	1.0	3.1	10	3.5
1.0	2.0	1.5	2.2	20	3.5
1.0	2.0	2.0	1.8	40	3.6

*$10^3[KIO_3]_0$=1.0 mol dm^{-3} ; $10^2[TSC]_0$=2.0 mol dm^{-3} ; $10[HClO_4]$=1.0 mol dm^{-3} ; μ=0.5 mol dm^{-3} (except during its variation) ; Temp.=303 K.

TABLE 3—PSEUDO-FIRST ORDER CONSTANTS (k_{obs}) FOR OXIDATION OF THIOSEMICARBAZIDE IN Zn^{II}-BOUND STATE BY POTASSIUM IODATE*

$[KIO_3]_0$ $\times 10^4$ mol dm^{-3}	$[Complex]_0$ $\times 10^3$ mol dm^{-3}	$[HClO_4]$ $\times 10$ mol dm^{-3}	k_{obs} $\times 10^4$ s^{-1}	μ mol dm^{-3}	k_{obs} $\times 10^4$ s^{-1}
1.0	4.0	1.06	2.7	0.11	3.2
2.0	4.0	1.06	2.7	0.2	3.0
4.0	4.0	1.06	2.7	0.3	2.7
8.0	4.0	1.06	2.7	0.5	2.6
2.0	1.0	1.06	2.5	% Methanol	
2.0	2.0	1.06	2.5	0	2.7
2.0	4.0	1.06	2.7	10	2.8
2.0	8.0	1.06	2.7	20	2.8
2.0	10.0	1.06	2.6	40	2.9
2.0	4.0	0.16	7.6	[KI] ($\times 10^3$ mol dm^{-3})	
2.0	4.0	0.26	5.9	0	2.7
2.0	4.0	0.46	4.1	1.0	2.9
2.0	4.0	1.06	2.7	5.0	3.2
2.0	4.0	2.06	1.8	10.0	3.5

*$10^4[KIO_3] = 2.0$ mol dm^{-3} ; 10^3[complex] = 4.0 mol dm^{-3} ; $10[HClO_4] = 1.06$ mol dm^{-3} ; $\mu = 0.30$ mol dm^{-3} (except during its variation) ; Temp. = 303 K.

TABLE 4—KINETIC DATA AND THERMODYNAMIC PARAMETERS FOR OXIDATION OF NCS^- AND THIOSEMICARBAZIDE IN FREE AND METAL-BOUND STATES BY KIO_3

Orders observed in	NCS^-	TSC	Complex
$[KIO_3]$	1.0	1.0	1.0
[S]	0.9	0.13	0
$[H^+]$	0	−0.7	−0.6
Parameters :			
log A	12.4	8 6	7.2
E_a (kJ mol^{-1})	89.3	70.5	64.3
$\Delta H^{\neq}$ (kJ mol^{-1})	86.9	67 9	61 8
$\Delta S^{\neq}$ (JK mol^{-1})	−1 8	−19.0	−25.6
$\Delta G^{\neq}$ (kJ mol^{-1})	87.4	73.7	69.6

were calculated at each temperature. The latter constants were employed to compute the activation parameters from the Arrhenius and Eyring plots (Table 4).

Mechanisms of oxidations :

Oxidation fo thiocyanate ion : Kinetics of first order in $[KIO_3]$, fractional order in $[NCS^-]$ and non-dependence of rate on $[H^+]$ may be explained by the mechanism shown in Scheme 1. It is quite likely that under present acidic conditions, oxidant and substrate exist in the forms HIO_3 and HNCS respectively.

$$HIO_3 + HNCS \overset{K_1}{\rightleftharpoons} (X) \qquad \text{(fast)}$$

$$(X) \xrightarrow{k_2} \text{Products} \qquad \text{(slow)}$$

Scheme 1

Based on Scheme 1, the rate law (3) has been deduced.

$$-\frac{d[HIO_3]}{dt} = \frac{K_1 k_2\,[HNCS][HIO_3]}{1 + K_1[HNCS]} \qquad (3)$$

or

$$k_{obs} = \frac{K_1 k_2 [HNCS]}{1 + K_1[HNCS]} \qquad (4)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{K_1 k_2 [HNCS]} + \frac{1}{k_2} \qquad (5)$$

The plots of $1/k_{obs}$ vs $1/[NCS^-]$ were linear (Fig. 1) in conformity with the rate law (5). The constants K_1 (22.5 dm^3 mol^{-1}) and k_2 (6.7×10^3 s^{-1}) were calculated from the slope and intercept of the plot.

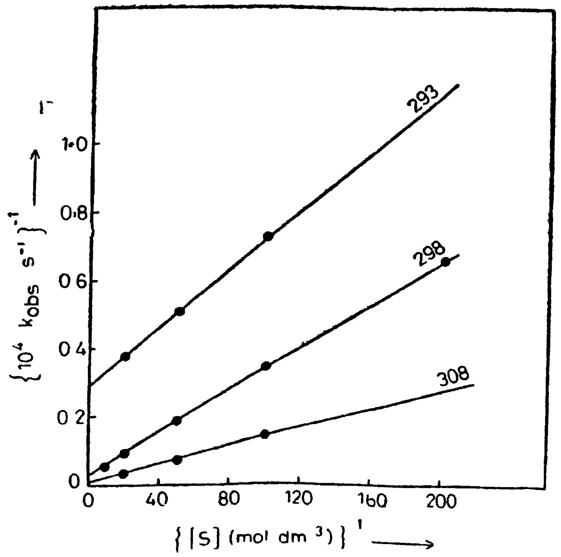

Fig. 1. Plot of $1/k_{obs}$ vs $1/[S]$ (S : NCS^-) at different temperatures ; $10^3[KIO_3]_0 = 1.0$ mol dm^{-3}. 10^3 $[HClO_4] = 5.0$ mol dm^{-3}, $\mu = 0.5$ mol dm^{-3}.

Oxidation of TSC in free state : The results of first order kinetics in [KIO_3], inverse fractional order in [H^+] and fractional order in [TSC] may be explained by Scheme 2.

$$HIO_3 \overset{K_3}{\rightleftharpoons} IO_3^- + H^+ \qquad \text{(fast)}$$

$$IO_3^- + (S) \overset{K_4}{\rightleftharpoons} \text{Intermediate (Y)} \qquad \text{(fast)}$$

$$(Y) \xrightarrow{k_5} (Y') \qquad \text{(slow)}$$

$$(Y') + IO_3^- \longrightarrow \text{Products} \qquad \text{(fast)}$$

Scheme 2

where, (S) is substrate TSC.

The rate law (equation 6) is in accordance with Scheme 2.

$$-\frac{d[HIO_3]}{dt} = \frac{K_3K_4k_5[HIO_3]_t[S]}{K_3+[H^+]+K_3K_4[S]} \tag{6}$$

or

$$k_{obs} = \frac{K_3K_4k_5[S]}{K_3+[H^+]+K_3K_4[S]} \tag{7}$$

or

$$\frac{1}{k_{obs}} = \frac{K_3+[H^+]}{K_3K_4k_5}\,\frac{1}{[S]}+\frac{1}{k_5} \tag{8}$$

or

$$\frac{1}{k_{obs}} = \frac{[H^+]}{K_3K_4k_5[S]}+\frac{1+K_4[S]}{K_4k_5[S]} \tag{9}$$

The plots of $1/k_{obs}$ vs $1/[S]$ and $1/k_{obs}$ vs [H^+] were linear (Fig. 2) in accordance with the rate law (8) or (9). The constant k_5 (3.4×10^4 s^{-1}) was calculated from the intercept of the former plot.

Oxidation of TSC in its metal complex : Oxidation of TSC in its metal complex by KIO_3 showed first order kinetics in [KIO_3], inverse fractional order in [H^+] and was independent of [complex]. The kinetic behaviour may be explained by the mechanism shown in Scheme 3.

$$HIO_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} IO_3^- + H^+ \qquad \text{(slow)}$$

$$IO_3^- + \text{complex} \longrightarrow \text{Products} \qquad \text{(fast)}$$

Scheme 3

Based on Scheme 3, the rate law (10) has been obtained.

$$-\frac{d[HIO_3]}{dt} = \frac{K_3k_3[HIO_3]}{K_3+[H^+]} \tag{10}$$

or

$$k_{obs} = \frac{K_3k_3}{K_3+[H^+]} \tag{11}$$

or

$$\frac{1}{k_{obs}} = \frac{[H^+]}{K_3k_3}+\frac{1}{k_3} \tag{12}$$

The plot of $1/k_{obs}$ vs [H^+] was linear (Fig. 2) in conformity with the rate law (12). From the intercept and slope of the plot constants k_3 and K_3 were calculated : $k_3 = 8.3 \times 10^4$ s^{-1} ; $k_{-3} = 1.4 \times 10^2$ dm^3 mol^{-1} s^{-1} and $K_3 = 0.06$ mol dm^{-3}. The metal complexation of the ligand TSC makes the rate independent of its concentration.

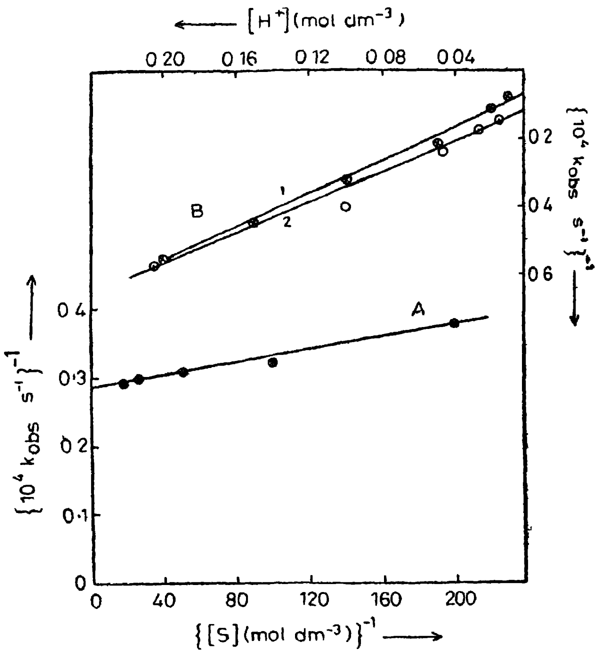

Fig. 2. (A) Plot of $1/k_{obs}$ vs $1/[S]$ (S : TSC), $10^3[KIO_3]_0 = 1.0$ mol dm^{-3}, $10[HClO_4]_0 = 1.0$ mol dm^{-3}, $\mu = 0.5$ mol dm^{-3}, temp. = 303 K. (B) Plot of $1/k_{obs}$ vs [H^+] : (1) $10^3[KIO_3]_0 = 1.0$ mol dm^{-3}, $10^2[TSC]_0 = 2.0$ mol dm^{-3}, $\mu = 0.5$ mol dm^{-3}, temp = 303 K, and (2) $10^4[KIO_3] = 2.0$ mol dm^{-3}, $10^3[complex]_0 = 4.0$ mol dm^{-3}, $\mu = 0.30$ mol dm^{-3}, temp. = 303 K.

The proposed mechanisms are supported by the moderate values of activation parameters. Negative values for the entropy of activation indicate the formation of activated complexes with a reduction in degrees of freedom.

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