

Kinetics and Mechanism of Oxidation of Thiocyanate Ion by Sodium N-Chloro-4-methyl Benzene Sulphonamide in Alkaline Medium

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Thiocyanate Ion, Chloramine-T

Kinetics of oxidation of potassium thiocyanate by the oxidant chloramine-T (CAT) in presence of NaOH has been studied at 30 °C. At low substrate concentrations, the approximate rate law is, $-d[\text{CAT}]/dt = k[\text{CAT}][\text{KNCS}]/[\text{NaOH}]^2$. At higher substrate concentrations, the rate law simplifies to, $-d[\text{CAT}]/dt = k[\text{CAT}]/[\text{NaOH}]$. Ionic strength and addition of *p*-toluene sulphonamide have negligible influence on the rate. The rate of reaction decreases in D₂O medium and the value of the inverse solvent isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ is 0.46. The reaction has been studied at different temperatures and the activation parameters have been calculated.

Introduction

Sodium N-chloro-4-methyl benzene sulphonamide, *p*-Me-C₆H₄SO₂NCINa · 3 H₂O, commonly called chloramine-T (CAT), behaves as an oxidising agent in both acidic and alkaline media. The oxidation potential of the CAT-sulphonamide system is pH dependent [1] and decreases with increase in pH of the medium. Although CAT has been widely used as a volumetric reagent in the determination of a variety of compounds, very few kinetic studies of these reactions are reported. The decomposition of H₂O₂ by CAT in the presence of HCl was the first reaction to be kinetically investigated by Coull and coworkers [2]. Recently, kinetics of chlorination of *p*-cresol [3], oxidation of glycerol [4], Os(VIII) catalysed oxidation of α -hydroxy acids [5], oxidation of ketones [6–8], aldehydes [9], sugars [10], alcohols [11–13], aminoacids [14, 15], dimethyl sulphoxide [16] and EDTA [17] have been reported. As a part of our mechanistic investigations of oxidation reactions of chloramine-T [11, 15, 16], we have studied the kinetics of oxidation of KNCS in aqueous solution by CAT. The reaction was rapid for rate measurements in acid and neutral solutions and hence the kinetic runs were made in alkaline medium ($\sim 10^{-2}$ – 10^{-3} M NaOH).

Sant [18] has reported the oxidation of thiocyanate ion with H₂O₂ in sulphuric acid medium. Wilson and Harris [19] have shown that the rate is

first order each in [H₂O₂] and [NCS[−]] and is independent on [H⁺] in the range 4 < pH < 12. However, in the presence of 0.05–1.3 M HClO₄, the rate [20] is directly proportional to [H⁺]. Similar results have been obtained by Csanyi and Horvath [21]. Briot and Smith [22] have oxidised NCS[−] ion with aqueous iodine in the pH range 9.2–12.5. The reaction is general base catalysed with an order unity with respect to [NCS[−]], [I₃[−]] and [OH[−]]. A strong inhibition of rate by iodide ion has been noted. Kinetics of oxidation of NCS[−] ion by Cr(VI) [23], V(V) [24], and Bi(V) [25] in acid medium has been reported.

Experimental

All solutions were prepared in triply distilled water. E. Merck KNCS was purified, and its aqueous solution (~ 1 M) was standardised by the argentometric method. Chloramine-T (E. Merck) was purified by the method of Morris *et al.* [26]. An approximately decimolar aqueous solution of this compound was prepared and standardised by the iodometric method. All other reagents were of accepted grades of purity. The ionic strength was kept constant at a high value by use of a concentrated solution of sodium perchlorate. Heavy water (99.4% D₂O) for solvent isotope effect studies was supplied by the Bhabha Atomic Research Centre, Trombay, India.

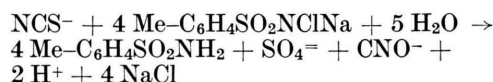
The reaction was carried out in a glass stoppered Pyrex boiling tube. Requisite amounts of thiocyanate solution, NaOH and NaClO₄ solutions and water (to keep the total volume constant for all runs) were taken in the tube and were thermostated at 30 °C. A measured amount of CAT solution also thermostated at the same temperature was added to the mixture in the boiling tube. The progress of the reaction was followed for two half lives by

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iodometric estimation of unreacted CAT in a measured aliquot of the reaction mixture at various time intervals. The pseudo first order rate constants calculated were reproducible to $\pm 3\%$.

Stoichiometry

Reaction mixtures containing excess CAT over KNCS were kept at room temperature ($27 \pm 3^\circ\text{C}$) in the presence of 10^{-2} M NaOH for 24 h. Estimation of the unchanged CAT showed that one mole of KNCS consumed four moles of CAT:



The presence of sulphate [27] and cyanate ions [28] among the reaction products was detected by the conventional tests. Paper chromatography was used to identify the sulphonamide ($R_f = 0.91$). Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent.

Results

a) Low substrate concentration (0.0025–0.02 M)

With a stoichiometric excess of [KNCS], plots of $\log [\text{CAT}]$ vs. time are found to be linear indicating first order dependence on [CAT] (Fig. 1 and Table I). The first order k values are sensitive to variations in substrate concentration (Table I). A plot of $\log k_1$ vs. $\log [\text{NCS}^-]_0$ gives a straight line with a slope of 0.86, indicating fractional order dependence of rate on [KNCS] (Fig. 2). Alkali retards the rate (Table II). A plot of $\log k_1$ vs. $\log [\text{OH}^-]$ gives a straight line of slope -1.9 (Fig. 3). Changing the ionic strength of the medium or addition of the reaction product, *p*-toluene sulphonamide (RNH_2) has little influence on the rate of reaction (Table III).

The reaction was carried out at different temperatures (30 – 50°C). The kinetic parameters are: $E_a = 63.2 \text{ KJ mole}^{-1}$; $\log A = 5.8$; $\Delta H^\ddagger = 60.7 \text{ KJ mole}^{-1}$; $\Delta S^\ddagger = -69.0 \text{ JK}^{-1}$; $\Delta G^\ddagger = 81.9 \text{ KJ mole}^{-1}$.

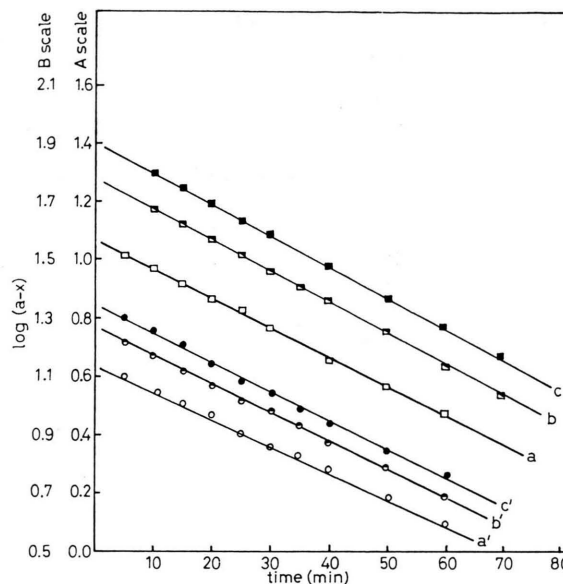


Fig. 1. First order rate plots at 30°C for the reaction of potassium thiocyanate with chloramine-T.

Scale A: $[\text{KNCS}]_0 = 0.01 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; $\mu = 0.5 \text{ M}$; $[\text{CAT}]_0$, (a) = 0.003 M ; (b) = 0.004 M ; (c) = 0.005 M .
Scale B: $[\text{KNCS}]_0 = 0.1 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; $\mu = 0.5 \text{ M}$; $[\text{CAT}]_0$, (a') = 0.003 M ; (b') = 0.004 M ; (c') = 0.005 M .

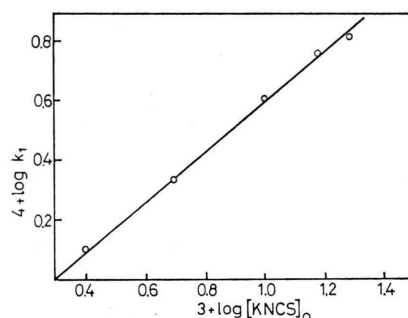


Fig. 2. Plot of $\log k_1$ against $\log [\text{KNCS}]_0$. $[\text{CAT}]_0 = 0.004 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; $\mu = 0.5 \text{ M}$; temp.: 30°C .

$10^3 [\text{CAT}]_0$	$10^2 [\text{KNCS}]_0$	$10^4 k_1$	$10^3 [\text{CAT}]_0$	$10^2 [\text{KNCS}]_0$	$10^4 k_1$
M	M	sec^{-1}	M	M	sec^{-1}
2.0	1.0	4.02	4.0	0.25	1.28
3.0	1.0	3.98	4.0	0.50	2.11
3.5	1.0	4.16	4.0	1.00	4.03
4.0	1.0	4.03	4.0	1.50	5.76
5.0	1.0	4.13	4.0	2.00	6.26

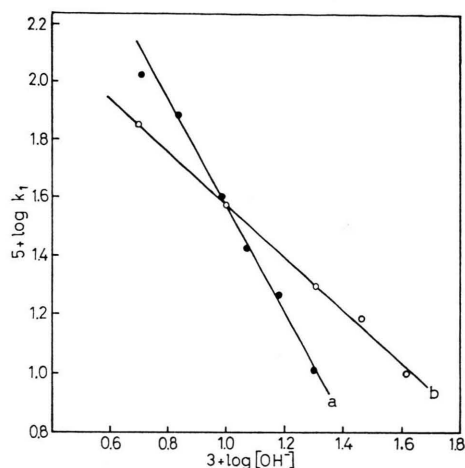
Table I. Kinetics of oxidation of potassium thiocyanate by chloramine-T. $[\text{NaOH}] = 0.01 \text{ M}$; $\mu = 0.5 \text{ M}$; temp.: 30°C .

Table II. Effect of sodium hydroxide concentration on the reaction rate. $[\text{KNCS}]_0 = 0.01 \text{ M}$; $[\text{CAT}]_0 = 0.004 \text{ M}$; $\mu = 0.5 \text{ M}$; temp.: 30°C .

$10^3 [\text{NaOH}]$ M	$10^4 k_1$ sec^{-1}
5.0	13.34
7.0	7.68
10.0	4.03
12.0	2.66
15.0	1.85
20.0	1.11

Tab. III. Effect of ionic strength and *p*-toluene sulphonamide on the reaction rate. $[\text{CAT}]_0 = 0.004 \text{ M}$; $[\text{KNCS}]_0 = 0.01 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; temp.: 30°C .

μ M	$10^4 k_1$ sec^{-1}	$10^3 [\text{PTS}]$ M	$10^4 k_1$ sec^{-1}
0.25	4.34	0.0	4.03
0.50	4.03	7.5	4.70
1.00	4.01	10.0	4.94

Fig. 3. Plot of $\log k_1$ against $\log [\text{OH}^-]$. $[\text{CAT}]_0 = 0.004 \text{ M}$; $\mu = 0.5 \text{ M}$; temp.: 30°C . (a) $[\text{KNCS}]_0 = 0.01 \text{ M}$; (b) $[\text{KNCS}]_0 = 0.1 \text{ M}$.*b) High substrate concentration (0.1–0.4 M)*

With the substrate in large excess, the rate is first order in CAT (Table IV and Fig. 1). The pseudo first order rate constants are insensitive to $[\text{KNCS}]$ (Table IV) and hence the rate is independent of substrate concentration. The rate decreases with $[\text{OH}^-]$ (Table V) and a plot of $\log k_1$ vs. $\log [\text{OH}^-]$ gives a straight line of slope-1 (Fig. 3). Ionic strength variations and addition of RNH_2 have no effect on the rate. Similarly, the effects of neutral salts, NaCl and KCl on the rate of reaction are small (Table VI).

Table V. Effect of sodium hydroxide concentration on the reaction rate. $\mu = 0.5 \text{ M}$; $[\text{KNCS}]_0 = 0.1 \text{ M}$; $[\text{CAT}]_0 = 4 \times 10^{-3} \text{ M}$; temp.: 30°C .

$10^3 [\text{NaOH}]$ M	$10^4 k_1$ sec^{-1}
5.0	6.91
10.0	3.84
20.0	1.92
30.0	1.60
40.0	0.96

$10^3 [\text{CAT}]_0$ M	$10 [\text{KNCS}]_0$ M	$10^4 k_1$ sec^{-1}	$10^3 [\text{CAT}]_0$ M	$10 [\text{KNCS}]_0$ M	$10^4 k_1$ sec^{-1}
3.00	1.0	3.59	4.0	1.5	3.77
3.25	1.0	3.70	4.0	2.0	3.74
3.50	1.0	3.77	4.0	2.5	3.74
3.75	1.0	3.80	4.0	3.0	3.77
4.00	1.0	3.84	4.0	4.0	3.88
4.25	1.0	3.85	—	—	—
4.50	1.0	3.92	—	—	—
5.00	1.0	3.97	—	—	—

Table IV. Kinetics of oxidation of potassium thiocyanate by chloramine-T. $\mu = 0.5 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; temp.: 30°C .

μ , M (PTS, M)	$10^4 k_1$ sec^{-1}	$10 [\text{NaCl}]$ M	$10^4 k_1$ sec^{-1}	$10 [\text{KCl}]$ M	$10^4 k_1$ sec^{-1}
0.50	3.84	0.0	2.69	0.0	2.69
(0.000)	3.84	0.2	3.00	0.2	3.01
0.75	3.83	0.4	3.01	0.4	3.26
(0.005)	3.15	0.6	3.01	0.6	3.39
1.00	3.97	0.8	3.04	0.8	3.45
1.50	4.30	1.0	3.07	1.0	3.52

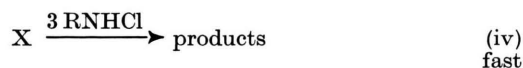
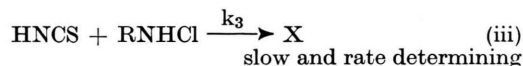
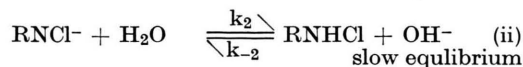
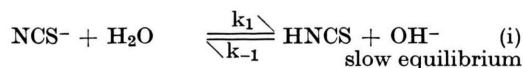
Table VI. Effect of neutral salts on the reaction rate. $[\text{CAT}]_0 = 0.004 \text{ M}$; $[\text{KNCS}]_0 = 0.1 \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$; temp.: 30°C .

The reaction was studied in D₂O medium. The values were, $(k_1)_{D_2O} = 1.76 \times 10^{-4} \text{ sec}^{-1}$ and $(k_1)_{H_2O} = 3.84 \times 10^{-4} \text{ sec}^{-1}$. The inverse solvent isotope effect was therefore 0.46.

The reaction was carried out at different temperatures. The activation parameters are: $E_a = 66.5 \text{ KJ mole}^{-1}$; $\log A = 6.09$; $\Delta H^\ddagger = 64.0 \text{ KJ mole}^{-1}$; $\Delta S^\ddagger = -64.4 \text{ JK}^{-1}$; $\Delta G^\ddagger = 83.5 \text{ KJ mole}^{-1}$.

Discussion

Chloramine-T (RNCINa where $R = p\text{-CH}_3\text{-C}_6\text{H}_4\text{SO}_2$) is a strong electrolyte [29] and the anion RNCl^- can be protonated in aqueous solution by mineral acids to give RNHCl . Hydrolysis of RNHCl yields HOCl in neutral solution, while its disproportionation produces dichloramine-T (RNCl_2). In aqueous alkaline solutions of the oxidant, HOCl and RNCl_2 do not exist but the reactive species are chloramine-T itself, NaOCl and RNHCl . During kinetic investigations on the oxidation of thioanisoles by CAT, Dell'Erba and Spinelli [30] observed a retarding influence of OH^- ions on the rate and suggested that RNHCl is the main oxidising species in alkali retarded chloraminometric reactions. This observation has been confirmed by Bernanose and Simon [31] and Mushran and coworkers [5, 6, 9, 14]. Scheme I has been proposed to account for the observed kinetics under low substrate concentrations.



Scheme I.

Assuming steady state for the intermediate species HNCS and RNHCl and making the reasonable assumption that $k_{-1}k_{-2}[\text{OH}^-]^2 \gg k_{-2}k_3[\text{RNHCl}][\text{OH}^-]$, the rate of disappearance of CAT can be shown as

$$-d[\text{CAT}]/dt = \frac{k_1 k_2 k_3 [\text{H}_2\text{O}]^2 [\text{CAT}][\text{KNCS}]}{k_{-1}k_{-2}[\text{OH}^-]^2 + k_1 k_3 [\text{KNCS}][\text{H}_2\text{O}]} \quad (1)$$

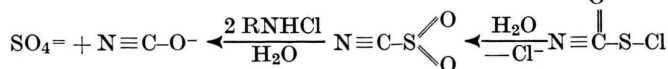
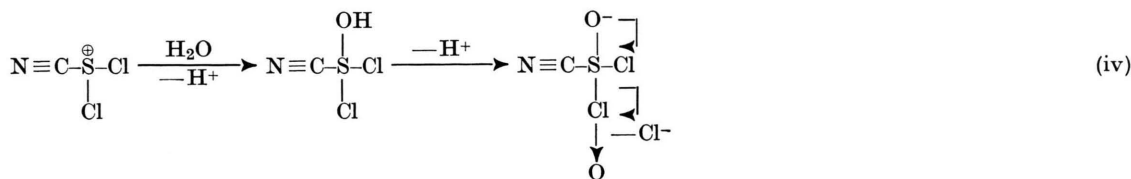
Since k_3 is small,

$$-d[\text{CAT}]/dt = \frac{k_1 k_2 k_3 [\text{H}_2\text{O}]^2 [\text{CAT}][\text{KNCS}]}{k_{-1}k_{-2}[\text{OH}^-]^2} \quad (2)$$

or

$$-d[\text{CAT}]/dt = \frac{k' [\text{CAT}][\text{KNCS}]}{[\text{OH}^-]^2} \quad (3)$$

in agreement with experimental results.



Scheme II.

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