

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

### **Oxidative conversion of thiourea and *N*-substituted thioureas into formamidine disulfides with acidified chloramine-T: a kinetic and mechanistic approach**

J. P. Shubha<sup>a</sup>; Puttaswamy<sup>a</sup>

<sup>a</sup> Department of Post-Graduate Studies in Chemistry, Central College Campus, Bangalore University, Bangalore, India

**To cite this Article** Shubha, J. P. and Puttaswamy(2009) 'Oxidative conversion of thiourea and *N*-substituted thioureas into formamidine disulfides with acidified chloramine-T: a kinetic and mechanistic approach', *Journal of Sulfur Chemistry*, 30: 5, 490 – 499

**To link to this Article:** DOI: 10.1080/17415990902725725

**URL:** <http://dx.doi.org/10.1080/17415990902725725>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Oxidative conversion of thiourea and *N*-substituted thioureas into formamidine disulfides with acidified chloramine-T: a kinetic and mechanistic approach

J.P. Shubha and Puttaswamy\*

Department of Post-Graduate Studies in Chemistry, Central College Campus, Bangalore University, Bangalore, India

(Received 21 October 2008; final version received 5 January 2009)

The kinetics of oxidation of thiourea and *N*-substituted thioureas namely: *N*-methylthiourea, *N*-allylthiourea *N*-phenylthiourea and *N*-tolylthiourea to the corresponding formamidine disulfides by sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) in the presence of HClO<sub>4</sub> has been investigated at 278 K. The reactions follow identical kinetics for all thioureas, being first order each with respect to [CAT]<sub>0</sub>, [Thiourea]<sub>0</sub> and [H<sup>+</sup>]. Ionic strength of the medium and addition of *p*-toluenesulfonamide or halide ions have negligible influence on the rate. The solvent isotope effect has been studied using D<sub>2</sub>O in the case of the oxidation of thiourea. Decrease in the dielectric constant of the medium by adding methanol decreases the rate. The reactions were studied at different temperatures, and the composite activation parameters have been computed. An isokinetic relationship was observed with  $\beta = 314$  K, indicating that enthalpy factors control the reaction rate. Under comparable experimental conditions, the rate of oxidation of thioureas increases in the order: *N*-allylthiourea > *N*-phenylthiourea > *N*-methylthiourea > thiourea > *N*-tolylthiourea. A mechanism involving the interaction of conjugate acid (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NHCl) and substrate giving an intermediate complex, in a slow step, has been suggested. The derived rate law is in agreement with the observed kinetics.

**Keywords:** thiourea and *N*-substituted thioureas; chloramine-T; oxidation-kinetics; mechanism; acid medium

### 1. Introduction

Sulfur compounds undergo a variety of metabolic reactions, namely oxidations, reductions, hydrolysis and conjugations (1). Thiourea is one of the simplest and most reactive sulfur compounds and one that exhibits complex non-linear behavior on being oxidized. It is a well known metal complexing agent and is used as a stabilizer and anti-oxidant for a number of compounds, such as vitamins, alkaloids and polymers. Thiourea and its derivatives are interesting compounds with a group of very active biological molecules and are widely used in the production of some pharmaceuticals (2–4). Thus, thiourea and its derivatives are extremely versatile chemicals, which find widespread application in industrial productions (5, 6). Thiourea, with two lone pairs of

\*Corresponding author. Email: pswamy\_chem@yahoo.com

electrons on the S atom, is the conspicuous choice to further substantiate the high reactivity of the species with a lone pair of electrons. The products of oxidation of thiourea depend on the type of oxidant used and on the reaction conditions (4, 7). Subsequently, the kinetic and mechanistic investigations of the oxidation of thiourea and its derivatives have been carried out by several groups of workers using a variety of oxidants (2, 5, 8–10). Organic *N*-haloamines have been used for estimating thiourea and its derivatives (11, 12) in solution, but there seems to be no report available in the literature on the oxidation of thiourea and substituted thioureas by these reagents from their kinetic and mechanistic view points. For these reasons, we have taken up a systematic kinetic study of the oxidation of thiourea and *N*-substituted thioureas, namely *N*-allylthiourea, *N*-methylthiourea, *N*-tolylthiourea and *N*-phenylthiourea by chloramine-T (CAT) in perchloric acid medium, in order to explore the mechanistic aspects of these oxidations.

The chemistry of organic *N*-haloamines has awakened considerable interest, as these compounds are sources of halonium cations, hypohalite species and *N*-anions which act both as bases and nucleophiles (13–16). Generally, these haloamines undergo a two-electron change in reactions forming the corresponding sulfonamide and sodium halide (13). They are capable of affecting an array of molecular transformations, including limited oxidation of specific groups. Chloramine-T (CAT  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa} \cdot 3\text{H}_2\text{O}$ ) is the most important member of organic *N*-haloamine family and behaves as an oxidizing agent in both acidic and alkaline media. The redox potential of CAT–*p*-toluenesulfonamide (PTS) couple is pH dependent (17) and decreases with the increase in pH of the medium (1.139 V at pH 0.65, 1.778 V at pH 7.0 and 0.614 V at pH 9.7). CAT is a mild, efficient, stable and inexpensive oxidant and the mechanistic aspects of many of its reactions have been well documented (13, 18–26). It was, therefore, of much interest to investigate the mechanism of oxidations of the selected thioureas with this reagent.

The present work was carried out with the following objectives: (1) to determine the kinetic data with respect to all variables; (2) to elucidate a plausible mechanism; (3) to design appropriate kinetic model; (4) to assess the relative rates of oxidation of thioureas towards CAT; (5) to ascertain the reactive species; (6) to identify the stoichiometry and oxidation products; and (7) to establish the isokinetic relationships using activation parameters.

## 2. Results and discussion

Our preliminary kinetic experiments revealed that the reactions between selected thioureas and CAT were too rapid to be measured in neutral, acidic or alkaline mediums at ambient temperature. Consequently, the mechanism and rate law for these redox systems were mysterious. Hence, to investigate the kinetic and mechanistic aspects of these reactions, detailed experiments were carried out at 278 K in acid medium ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), and optimum conditions for the formation of formamidine disulfides were established. These formamidine disulfides are useful compounds in the extraction of gold as an oxidizing agent and accelerators in electroplating. The experimental results indicate that the kinetic behavior of oxidation of these thioureas by CAT in  $\text{HClO}_4$  medium is similar.

### 2.1. Effect of varying reactant concentrations on the rate of the reaction

The kinetics of oxidation of aforementioned thioureas by CAT was investigated at different initial concentrations of the reactants. When the substrate is in large excess at constant  $[\text{Thiourea}]_0$ ,  $[\text{HClO}_4]$  and temperature, plots of  $\log [\text{CAT}]$  against time are found to be linear ( $r > 0.9849$ ). The pseudo first-order rate constants,  $k'$ , calculated are almost constant at different initial concentrations of CAT (Table 1). Hence, the rate of disappearance of CAT obeys first-order kinetics.

Table 1. Effects of varying oxidant, substrate and HClO<sub>4</sub> concentrations on the rate of the reaction at 278 K.

10 <sup>3</sup> [CAT] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>2</sup> [Thiourea] <sub>0</sub> (mol dm <sup>-3</sup> )	10 <sup>4</sup> <i>k'</i> (s <sup>-1</sup> )					
		10 <sup>4</sup> [HClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	<i>N</i> -tolyl thiourea	Thiourea	<i>N</i> -methyl thiourea	<i>N</i> -phenyl thiourea	<i>N</i> -allyl thiourea
0.5	1.5	1.0	6.75	8.80	11.3	11.8	16.4
1.0	1.5	1.0	6.77	8.97	10.8	12.6	15.9
1.5	1.5	1.0	6.81	8.91	11.1	12.3	16.2
2.0	1.5	1.0	6.80	9.20	11.4	12.7	16.8
3.0	1.5	1.0	6.78	8.76	10.6	11.6	15.5
4.0	0.5	1.0	2.46	2.90	4.39	4.68	5.41
1.5	1.0	1.0	4.86	6.28	8.30	8.97	10.8
1.5	1.5	1.0	6.81	8.91	11.1	12.3	16.2
1.5	2.0	1.0	8.91	11.2	15.4	16.4	22.4
1.5	3.0	1.0	13.0	16.6	23.2	24.3	34.0
1.5	1.5	0.2	1.32	2.13	2.07	2.25	3.67
1.5	1.5	0.5	3.25	4.44	5.17	5.76	7.56
1.5	1.5	1.0	6.81	8.91	11.1	12.3	16.2
1.5	1.5	1.5	10.1	12.8	15.1	16.9	21.9
1.5	1.5	2.0	13.6	17.6	20.9	24.8	31.7

It is seen that the value of *k'* increases with increase in concentration of thiourea (Table 1) and plots of log *k'* against log [Thiourea] are linear (*r* > 0.9954) with unit slopes. Hence, the reaction is first-order with respect to [Thiourea]<sub>0</sub>. Further, plots of *k'* against [Thiourea]<sub>0</sub> are almost linear (*r* > 0.9783) passing through origin, confirming the first-order dependence on [Thiourea]<sub>0</sub>, and also showing that the Thiourea–CAT complex has only transient existence. Furthermore, second-order rate constants *k''* = *k'*/[Thiourea], are nearly the same for all the thioureas, establishing the first-order dependence on thiourea concentration (values are not reported).

## 2.2. Effect of varying perchloric acid concentration on the rate of the reaction

Table 1 shows that at constant [CAT]<sub>0</sub> and [Thiourea]<sub>0</sub>, values of *k'* increased with increase in [HClO<sub>4</sub>] (Table 1). Plots of log *k'* against log [HClO<sub>4</sub>] were linear (*r* > 0.9806) with unit slopes, indicating a first-order dependence on the rate of [HClO<sub>4</sub>].

## 2.3. Effect of varying dielectric constant on the rate of the reaction

The dielectric constant (*D*) of the medium was varied by adding MeOH (0–20% v/v) to the reaction mixture, with all other experimental conditions being held constant. The rate was found to decrease with increase in MeOH content (Table 2) and plots of log *k'* against 1/*D* were linear (Figure 1; *r* > 0.9943) with negative slopes. It was further noticed that there was no reaction of the dielectric with the oxidant under the experimental conditions employed. The values of dielectric constant of CH<sub>3</sub>OH–H<sub>2</sub>O mixtures reported in the literature (27) were used.

## 2.4. Effect of solvent isotope on the rate of the reaction

As the oxidations of thioureas by CAT were accelerated by [H<sup>+</sup>], the solvent isotope effect was studied in D<sub>2</sub>O as the solvent medium, with thiourea as a probe. Values of *k'* (H<sub>2</sub>O) and *k'* (D<sub>2</sub>O) were 8.91 × 10<sup>-4</sup> s<sup>-1</sup> and 12.5 × 10<sup>-4</sup> s<sup>-1</sup>, giving a solvent isotope effect *k'* (H<sub>2</sub>O)/*k'* (D<sub>2</sub>O) = 0.71.

Table 2. Effects of varying dielectric constant ( $D$ ) of medium on the rate of the reaction at 278 K.

% CH <sub>3</sub> OH v/v	$D$	$10^4 k'$ (s <sup>-1</sup> )				
		<i>N</i> -tolyl thiourea	Thiourea	<i>N</i> -methyl thiourea	<i>N</i> -phenyl thiourea	<i>N</i> -allyl thiourea
0	76.7	6.21	8.91	11.1	12.3	16.2
5	74.5	5.92	7.34	8.77	10.4	12.0
10	72.4	4.97	5.89	7.58	8.74	10.4
15	69.7	4.23	4.63	6.41	7.28	8.20
20	67.5	3.58	3.10	5.07	6.05	6.44

Note: [CAT]<sub>0</sub> =  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup>; [Thiourea]<sub>0</sub> =  $1.5 \times 10^{-2}$  mol dm<sup>-3</sup>; [HClO<sub>4</sub>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>.

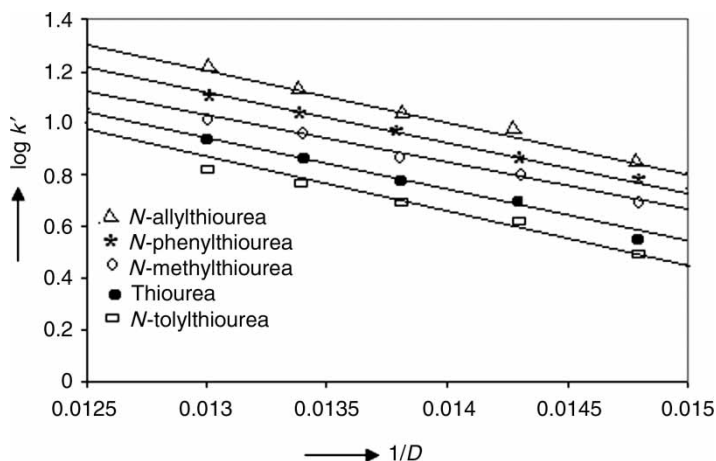


Figure 1. Plots of  $\log k'$  against  $1/D$ . Experimental conditions are as in Table 2.

### 2.5. Effect of PTS and halide ions on the rate of the reaction

Addition of PTS ( $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>), the reduction product of CAT, to the reaction mixture did not affect the rate significantly. This indicates that PTS is not involved in any step prior to the rate limiting step in the proposed scheme. Similarly, addition of Cl<sup>-</sup> or Br<sup>-</sup> ions in the form of NaCl or NaBr ( $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>) had no effect on the rate, signifying that no interhalogen or free chlorine is formed in the reaction sequence and the conjugate acid, TsNHCl, interacts directly with the substrate species in the slow and rate limiting step.

### 2.6. Effect of ionic strength on the rate of the reaction

The effect of ionic strength of the medium on the rate of reaction was carried out at 0.2 mol dm<sup>-3</sup> using NaClO<sub>4</sub> solution, with all other experimental conditions held constant. It was found that ionic strength had a negligible effect on the reaction rate, suggesting that non-ionic species are involved in the rate limiting step. Subsequently, the ionic strength of the reaction mixture was not fixed as constant for kinetic runs.

### 2.7. Effect of varying temperature on the rate of the reaction

The effect of temperature on the rate was studied by performing the kinetic runs at different temperatures (275–293 K), keeping other experimental conditions constant. From the linear Arrhenius

Table 3. Effects of varying temperature on the rate of the reaction and activation parameters for the oxidation of thioureas by CAT in HClO<sub>4</sub> medium.

Temperature (K)	$10^4 k' (\text{s}^{-1})$				
	<i>N</i> -tolyl thiourea	Thiourea	<i>N</i> -methyl thiourea	<i>N</i> -phenyl thiourea	<i>N</i> -allyl thiourea
275	4.25	6.95	8.68	9.20	14.2
278	6.81	8.91	11.1	12.3	16.2
283	8.90	11.8	14.0	13.7	19.9
288	13.2	15.1	16.2	16.6	22.6
293	20.2	18.4	20.5	20.8	29.4
$E_a$ (kJ mol <sup>-1</sup> )	51.0	35.4	29.2	28.4	23.9
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	48.7	33.0	26.8	26.1	21.6
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	85.7	85.3	84.8	84.8	84.0
$\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )	-130	-184	-205	-207	-220
log A	12.2	9.40	8.34	8.21	7.53

Note: [CAT]<sub>0</sub> =  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup>; [Thiourea]<sub>0</sub> =  $1.5 \times 10^{-2}$  mol dm<sup>-3</sup>; [HClO<sub>4</sub>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>.

plots of log  $k'$  against  $1/T$  ( $r > 0.9982$ ), values of activation parameters ( $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  and log A) were computed, and these results are summarized in Table 3.

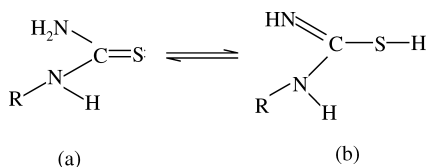
## 2.8. Test for free radicals

The addition of an aqueous solution of acrylamide to the reaction mixture did not cause polymerization. This suggests the absence of free radical involvement during the oxidation. Proper control experiments were also run simultaneously.

## 2.9. Reactive species of CAT and thiourea

CAT (TsNCINa) behaves like a strong electrolyte (14) in aqueous solutions, and depending on the pH of the medium, CAT furnishes different types of equilibria in solutions (14–16, 28–29). The probable oxidizing species in acidified CAT solutions are TsNHCl, TsNCl<sub>2</sub>, HOCl and possibly H<sub>2</sub>OCl<sup>+</sup>. If TsNCl<sub>2</sub> were to be the reactive species, then the rate law predicts a second-order dependence of rate on CAT, which is contrary to experimental observations. If HOCl is involved, a first-order retardation of rate by the added PTS is expected. However, no such effect was noticed. The rate dependence on [H<sup>+</sup>] indicates the protonation of CAT and has been thoroughly investigated (15, 16). First-approximation calculations by Bishop and Jennings (14) on decinormal solutions of CAT have shown that concentrations of TsNHCl and HOCl are approximately 10<sup>-2</sup> and 10<sup>-7</sup> mol dm<sup>-3</sup>, respectively, around pH 0–1. Therefore, in the present case, it is likely that the conjugate acid itself, TsNHCl, acts as the reactive oxidant species interacting with thiourea.

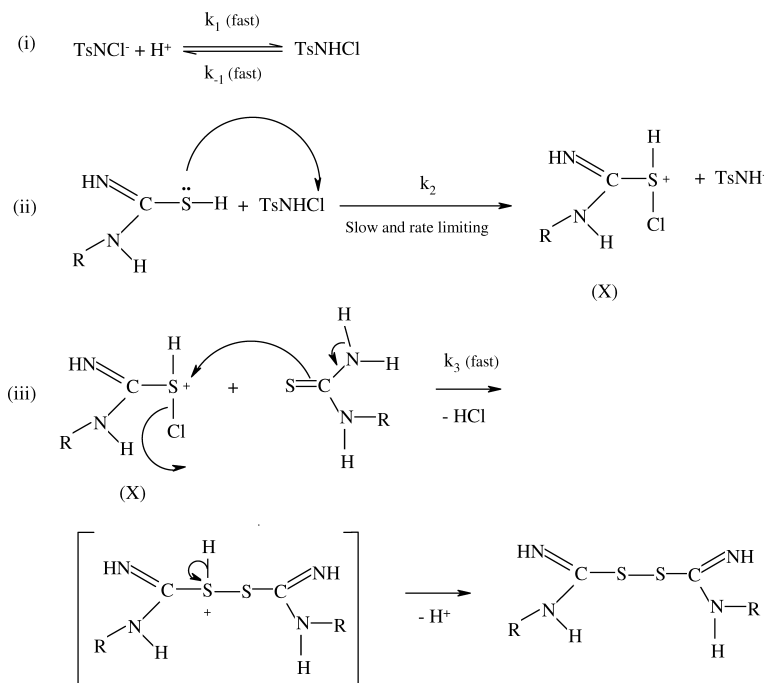
Thiourea exhibits isomerism as shown below:



In the present case, both (a) and (b) forms of thiourea are involved in the reaction.

## 2.10. Reaction scheme and rate law

In view of preceding discussion and experimental data, the following mechanism (Scheme 1) is proposed for the thiourea oxidation by CAT in  $\text{HClO}_4$  medium:



Scheme 1.

Here  $\text{Ts} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$  and  $\text{R} = -\text{H}$  for thiourea,  $-\text{CH}_3$  for *N*-methylthiourea,  $-\text{CH}_2-\text{CH}=\text{CH}_2$  for *N*-allylthiourea,  $-\text{C}_6\text{H}_5$  for *N*-phenylthiourea and  $-\text{C}_6\text{H}_4\text{CH}_3$  for *N*-tolylthiourea.

CAT ( $\text{TsNCINa}$ ) ionizes (14–16) in aqueous solutions (9–11) ( $\text{TsNCINa} \rightleftharpoons \text{TsNCl}^- + \text{Na}^+$ ) and the anion  $\text{TsNCl}^-$  in a fast initial equilibrium step can be protonated in acid medium to give the conjugate acid  $\text{TsNHCl}$  (step (i) of Scheme 1). In the next slow and rate limiting step (ii), a lone pair of electrons on the sulfur atom in the tautomeric form (b) of thiourea attacks the positive chlorine of  $\text{TsNHCl}$  to form a complex cation X. In the next fast step, the intermediate X reacts with another mole of substrate (form (a)) to give a highly unstable sulfonium ion intermediate with the elimination of  $\text{HCl}$ , which may lose a proton instantaneously to yield the final product, formamidine disulfide.

Scheme 1 envisages the direct participation of  $\text{TsNHCl}$  in a rate limiting step with the substrate. Assuming steady-state conditions for  $\text{TsNHCl}$  and with the reasonable approximation that  $k_{-1} \gg k_2 [\text{Thiourea}]$ , the rate law

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{CAT}] [\text{Thiourea}] [\text{H}^+]$$

can be derived in agreement with experimental results.

The proposed scheme and the derived rate law can explain the observed experimental results.

### 2.11. Solvent isotope effect

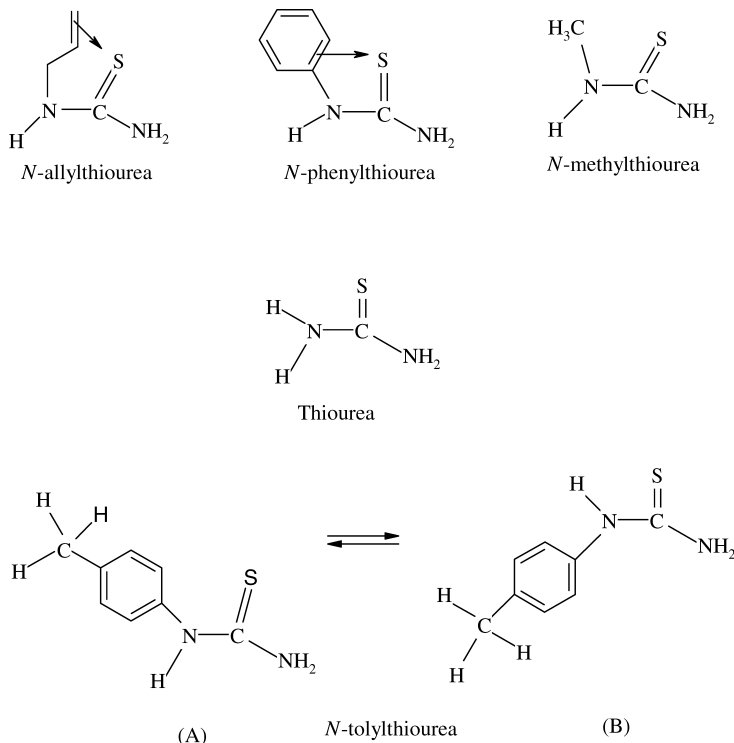
As expected for  $H^+$  catalyzed reactions, the rate increased in  $D_2O$  medium. For a reaction involving a fast pre-equilibrium  $H^+$  or  $OH^-$  ion transfer, the rate increases in  $D_2O$  medium since  $D_3O^+$  and  $OD^-$  are a stronger acid and a stronger base, respectively, than  $H_3O^+$  and  $OH^-$  ions (30, 31). Hence, the proposed mechanism is also supported by the increase of rate of reaction in  $D_2O$  medium.

### 2.12. Dielectric constant effect

Several approaches have been put forward to explain quantitatively the effect of the dielectric constant of the medium on the rates of reactions in solutions. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis (32) has shown that a plot of  $\log k'$  against  $1/D$  gives a straight line with a negative slope (Figure 1;  $r > 0.9943$ ) for the reaction between a negative ion and a dipole or between two dipoles, while a positive slope indicates a reaction between a positive ion and a dipole. The negative dielectric effect in the present studies are in agreement with dipole-dipole nature of the rate limiting step in the proposed scheme, and the reaction pathways suggested explain the kinetic results (32, 33).

### 2.13. Correlation of structure and reactivity

From an inspection of rate data (Table 3), the rate of oxidation of *N*-substituted thioureas follows the order: *N*-allylthiourea > *N*-phenylthiourea > *N*-methylthiourea > thiourea >





*N*-tolylthiourea. The reactivity of *N*-allylthiourea is highest as compared to other thioureas studied because the interaction of the  $\pi$  electrons in the allyl group, which increases the electron density on sulfur as shown below. In the case of *N*-tolylthiourea, the least reactivity is attributed to the probable existence of the stereo isomeric forms A and B. The observed rate, therefore, refers to the reaction of the B form of the *N*-tolylthiourea, which decreases the electron availability on sulfur and hence it is found to be least reactive among of all the thioureas studied. *N*-phenylthiourea is found to be more reactive than *N*-methylthiourea due to the mesomeric effect of the phenyl group. *N*-methylthiourea is faster as compared to thiourea, because of the +I effect of methyl group. Therefore, the overall reactivity of these thioureas has been justified.

### 2.14. Isokinetic relationship

The activation energy is highest for the slowest reaction and *vice versa* (Table 3), indicating that the reaction is enthalpy controlled. This is verified by calculating the isokinetic temperature  $\beta$  from the slope of the linear plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  (Figure 2;  $r = 0.9994$ ),  $\beta$  is found to be 314 K. The relationship was proved to be genuine through the Exner criterion (34) by plotting  $\log k'_{(283\text{ K})}$  against  $\log k'_{(275\text{ K})}$ , (Figure 2;  $r = 0.9989$ ). The value of  $\beta$  was calculated from the equation  $\beta = T_1(1 - q)/(T_1/T_2 - q)$ , where  $q$  is the slope of the Exner plot;  $\beta$  was found to be 306 K. It can be seen that the values of  $\beta$  are higher in both of the cases than the experimental temperature (278 K), indicating the enthalpy controlled nature of the reactions. The proposed mechanism is also supported by the moderate values of energy of activation and thermodynamic parameters (Table 3). The fairly high positive values of  $\Delta G^\ddagger$  and  $\Delta H^\ddagger$  indicate that the transition state is highly solvated while the large negative values of  $\Delta S^\ddagger$ , suggests the formation of a rigid associative transition state with a reduction in the degrees of freedom of molecules in each case. The constancy of  $\Delta G^\ddagger$  values indicates that all the five thioureas react with CAT via the same mechanism. Further, the experimental observation shows that there is no effect of PTS, halide ions and ionic strength on the reaction rate which also substantiates the proposed mechanism and the derived rate law.

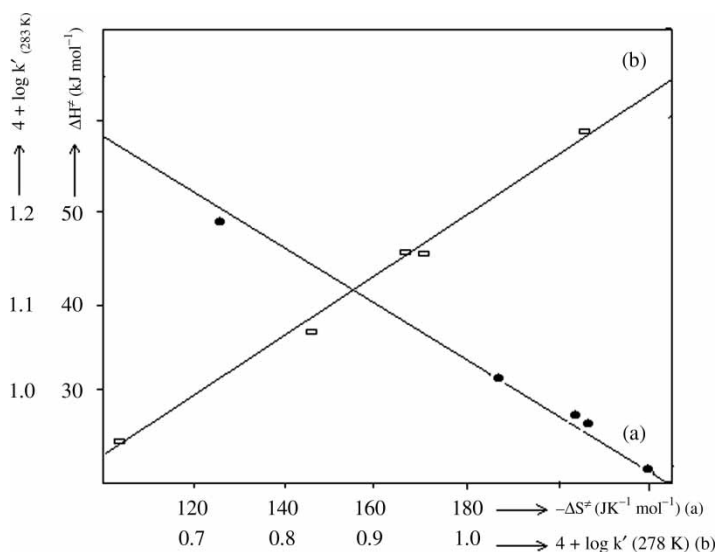


Figure 2. Isokinetic plots of (a)  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  and (b)  $\log k'_{(283\text{ K})}$  against  $\log k'_{(278\text{ K})}$ . Experimental conditions are as in Table 3.

### 3. Conclusion

The rate of oxidation of thiourea and *N*-substituted thioureas, viz. *N*-methylthiourea, *N*-allylthiourea, *N*-phenylthiourea and *N*-tolylthiourea by CAT in HClO<sub>4</sub> medium follows identical kinetics with a rate law  $-d[\text{CAT}]/dt = k [\text{CAT}]_0 [\text{Thiourea}]_0 [\text{H}^+]$ . Activation parameters have been evaluated. The value of isokinetic temperature ( $\beta = 314 \text{ K}$ ) obtained indicates that the oxidation of all thioureas with CAT is an enthalpy controlled reaction and the operation of an identical mechanism in the oxidation of aforesaid thioureas. The rate of oxidation of thioureas increased in the order: *N*-allylthiourea > *N*-phenylthiourea > *N*-methylthiourea > thiourea > *N*-tolylthiourea. A suitable reaction scheme is proposed and an appropriate rate law is deduced to account for the observed kinetic data.

### 4. Experimental

CAT (Merck) was purified by the method of Morris *et al.* (15). An aqueous solution of CAT was prepared, standardized by iodometric procedure and stored in amber colored stoppered bottles until further use, to prevent any photochemical degradation. The concentration of the stock solution was periodically determined. All the thioureas were of an acceptable grade of purity (Aldrich) and were used as received. Aqueous solutions of the compounds were used for kinetic studies. Heavy water (D<sub>2</sub>O, 99.4%), employed for solvent isotope studies, was obtained from the Bhabha Atomic Research Centre, Mumbai, India. All other chemicals were of analytical grade and double distilled water was used throughout the work.

Kinetic experiments were performed under pseudo first-order conditions of [substrate]<sub>0</sub> over [oxidant]<sub>0</sub>. The experimental procedure followed was identical to that reported earlier (24). The course of the reaction was studied for at least two half-lives. The pseudo first-order rate constants ( $k' \text{ s}^{-1}$ ), calculated from linear plots of  $\log [\text{CAT}]$  against time, were found to be reproducible within  $\pm 5\%$ . The regression coefficient ( $r$ ) was performed using a fx-100 W statistical calculator.

### 5. Stoichiometry

Different reaction mixtures containing different concentrations of CAT and substrate with constant HClO<sub>4</sub> concentration ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) were kept for about 24 h at 278 K and then analyzed. Iodometric titration of unreacted CAT showed that the oxidation of all the thioureas involves a single electron change with CAT. The observed stoichiometry is shown by Equation (1).



Here R = H for thiourea,  $-\text{CH}_3$  for *N*-methylthiourea,  $-\text{CH}_2-\text{CH}=\text{CH}_2$  for *N*-allylthiourea,  $-\text{C}_6\text{H}_4\text{CH}_3$  for *N*-tolylthiourea,  $-\text{C}_6\text{H}_5$  for *N*-phenylthiourea and Ts =  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$ .

### 6. Product analysis

The reactions of all five thioureas with CAT, separately in the stoichiometric ratio under stirred condition in presence of HClO<sub>4</sub> ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), were allowed to progress for 24 h at 278 K. After completion of the reaction (monitored by TLC), the reaction products were neutralized with NaOH and extracted with ether. The organic products were subjected to spot tests

and chromatographic analysis (TLC technique), which revealed the formation of corresponding formamidine disulfides as the oxidation products of *N*-substituted thioureas and PTS ( $\text{TsNH}_2$ ) as the reduction product of CAT. These oxidation products were separated by column chromatography on silica gel (60–120 mesh) using *n*-butanol and ethyl acetate (3:5 v/v) as the mobile phase.

The formation of formamidine disulfide, the oxidation product of thiourea, was confirmed by IR spectrum. IR spectrum was recorded on a Nicolet model impact 400 D FT-IR spectrum (KBr pellets  $3\text{ cm}^{-1}$  resolution). IR spectral bands of formamidine disulfide were observed at  $473\text{ cm}^{-1}$  for the S–S stretch (expected;  $450\text{--}550\text{ cm}^{-1}$ ),  $3240\text{ cm}^{-1}$  and  $2995\text{ cm}^{-1}$  for the  $-\text{NH}_2$  stretch,  $1662\text{ cm}^{-1}$  for the C=N stretch (expected;  $1660\text{ cm}^{-1}$ ) and  $700\text{ cm}^{-1}$  for the C–S stretch (expected;  $600\text{--}800\text{ cm}^{-1}$ ). It was further confirmed by gas chromatography coupled with mass spectrophotometry (GC–MS). The mass spectrum showed a parent ion peak at 150 amu, clearly confirming formamidine disulfide. PTS was also confirmed by GC–MS analysis; its mass spectrum showed a molecular ion peak at 171 amu. All the peaks observed in GC–MS can be interpreted in accordance with the observed structure. It was also noticed that there was no further oxidation of these products under prevailing kinetic conditions.

## Acknowledgement

The authors are thankful to Prof. M.A. Pasha for his valuable suggestions.

## References

- (1) Park, S.B.; Howald, W.N.; Cashman, J.R. *Chem. Res. Toxicol.* **1994**, *7*, 191–197.
- (2) Chigwada T.R.; Chikwana, E.; Simoyi, R.H. *J. Phys. Chem. A* **2005**, *109*, 1081–1093.
- (3) Mamaeva, E.A.; Bakibaev, A.A. *Tetrahedron* **2003**, *59*, 7521–7525.
- (4) Kelner, M.J.; Bagnell, R.; Welch, K.J. *J. Biol. Chem.* **1990**, *265* 1306–1311.
- (5) Kudrik, E.V.; Theodoridis, A.; Eldik, R.V.; Makarov, S.V. *Dalton Trans.* **2005**, 1117–1122.
- (6) Jagodzinski, T.S. *Chem. Rev.* **2003**, *103*, 197–227.
- (7) Li, J.; Miller, J.D. *Hydrometallurgy* **2002**, *63*, 215–223.
- (8) Hoffmann, M.; Edwards, J.O. *Inorg. Chem.* **1997**, *16*, 3333–3337.
- (9) Kulkarni, M.J.; Rao, B.M. *J. Indian Chem. Soc.* **1995**, *72*, 235–239.
- (10) Mehrotra, M.; Mehrotra, R.N. *Dalton Tran.* **2003**, 3606–3611.
- (11) Singh, B.; Verma, B.C.; Kalia, Y.K. *J. Indian Chem. Soc.* **1963**, *40*, 697–699.
- (12) Ahmed, M.S.; Mahadevappa, D.S. *Indian J. Chem.* **1979**, *18A*, 89–90.
- (13) Campbell, M.M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65–79.
- (14) Bishop, E.; Jennings, V.J. *Talanta* **1959**, *1*, 197–199.
- (15) Morris, J.C.; Salazar, J.A.; Wineman, M.A. *J. Am. Chem. Soc.* **1948**, *70*, 2036–2041.
- (16) Higuchi, T.; Ikeda, K.; Hussain, A. *Chem. Soc. B.* **1967**, 546–552.
- (17) Murthy, A.R.V.; Rao, B.S. *Proc. Indian Acad. Sci.* **1952**, *35*, 69–72.
- (18) Banerji, K.K.; Jayaram, B.; Mahadevappa, D.S. *J. Sci. Ind. Res.* **1987**, *46*, 65–76.
- (19) Ramachandra, H.; Rangappa, K.S.; Mahadevappa, D.S.; Gowda, N.M.M. *Monatsh. Chem.* **1996**, *127*, 241–255.
- (20) Armesto, X.L.; Canle, L.; Garia, M.V.; Santaballa, J.A. *Chem. Soc. Rev.* **1998**, *27*, 453–460.
- (21) Hegde, A.C.; Gowda, B.T. *Oxid. Commun.* **2000**, *23*, 546–564.
- (22) Saldanha, R.J.D.; Ananda, S.; Venkatesha, B.M.; Gowda, N.M.M. *J. Mol. Struct.* **2002**, *606*, 147–154.
- (23) Kambo, N.; Upadhyay, S.K.; Jain, A.K. *Oxid. Commun.* **2003**, *26*, 502–509.
- (24) Puttaswamy; Jagadeesh, R.V. *Int. J. Chem. Kinet.* **2005**, *37*, 201–210.
- (25) Puttaswamy; Jagadeesh, R.V. *Ind. Eng. Chem. Res.* **2006**, *45*, 1563–1570.
- (26) Puttaswamy; Vinod, K.N.; Gowda, K.N.N. *Dyes Pigments* **2008**, *78*, 131–138.
- (27) Akerloff, G.J. *Am. Chem. Soc.* **1932**, *54*, 4125–4135.
- (28) Hardy, F.F.; Johnston, J.P. *J. Chem. Soc. Perkin Trans. II* **1973**, 742–750.
- (29) Pryde, B.G.; Soper, F.G. *J. Chem. Soc.* **1962**, 1582–1588.
- (30) Collins, C.J.; Bowman, N.S. *Isotope Effects in Chemical Reactions*; Van Nostrand Reinhold: New York, 1970; p 267.
- (31) Kohen, A.; Limbach, H.H. *Isotope Effects in Chemistry and Biology*; CRC Press: Florida, 2006; pp 827–844.
- (32) Amis, E.S. *Solvent Effects on Reaction Rates and Mechanisms*; Academic Press: New York, 1966; p 1672.
- (33) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: New York, 2003; pp 219–237.
- (34) Exner, O. *Chem. Commun.* **1964**, *29*, 1094–1113.