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Reactivities of Ketone Thiosemicarbazones towards Chloramine-T: A Mechanistic Study

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Kinetics of oxidation of thiosemicarbazones by chloramine-T in 30% aqueous acetic acid medium in the presence of perchloric acid has been investigated at 293 K.The rate has first-order dependence in [CAT], fractional order in [Substrate] and inverse fractional order in [H_3O^+]. Addition of the reaction product, *p*-toluene sulphonamide and variation of ionic strength of the medium have no effect on the rate. An increase in the rate is observed with the decrease in dielectric constant of the medium. Activation parameters have been evaluated from the Eyring plots.The stoichiometric studies reveal that the reactants react in 1 : 5 mole ratio *via* the formation of a complex.

Key Words: Kinetic, Mechanistic, Chloramine-T, Oxidation, Alkanone thiosemicarbazones.

INTRODUCTION

Chloramine-T (CAT) has been widely used as an effective oxidant for the oxidation of amino acids,[1] alcohols[2, 3], aldehydes and ketones in both acidic and alkaline media[4–6], hexacyanoferrate (III)[7], alkanone semicarbazones in acidic media[8]. CAT interacts with a wide range of functional groups both as a chlorinating and oxidizing agent in aqueous and partially aqueous media in the presence of acids and alkalis.

In the present study, the kinetics of oxidation of a few aliphatic ketone thiosemicarbazones by CAT has been investigated with a view to propose a suitable mechanism and rate law and correlate the reactivity of various substrates with their structures.

EXPERIMENTAL

AnalaR grade (E. Merck, GR) chloramine-T is purified by the method of Morris *et al.*[9] Thiosemicarbazide (SRL) is used after recrystallization. Other reagents like perchloric acid, acetic acid, sodium perchlorate used were of excellar grade. The samples of propanone thiosemicarbazone (**1**), butanone thiosemi-

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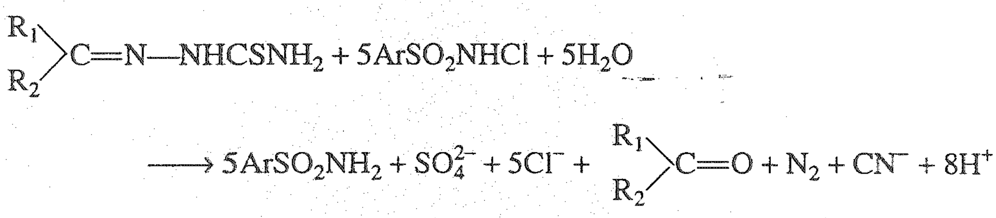
carbazone (**2**), 3-pentanone thiosemicarbazone (**3**) were prepared by reacting requisite amounts of respective ketones and thiosemicarbazides. The kinetic measurements were initiated by the rapid addition of appropriate volume of oxidant solution, thermally equilibrated at the desired temperature, to a mixture containing known amounts of substrate in acetic acid-water mixture in presence of $HClO_4$ pre-equilibrated at the same temperature. The progress of the reaction was monitored by iodometric estimation of unreacted oxidant at regular intervals of time.The stoichiometry of the reaction is determined by treating the substrate with known excess of the oxidant, allowing sufficient time for completion of the reaction at 293 K. The products of the reaction were identified by the standard tests.



$$\begin{matrix}R_1\\R_2\end{matrix}\!>C{=}N{-}NHCSNH_2 + 5ArSO_2NHCl + 5H_2O \longrightarrow 5ArSO_2NH_2 + SO_4^{2-} + 5Cl^- + \begin{matrix}R_1\\R_2\end{matrix}\!>C{=}O + N_2 + CN^- + 8H^+$$

RESULTS AND DISCUSSION

The kinetic dependence of rate on [CAT] is studied by varying [CAT] at constant [substrate] and [H_3O^+].The pseudo first order rate constant k_1 remains constant with variation of [CAT] indicating that the order with respect to [CAT] is unity. This is evidenced by the linear plots by log [CAT}$_T$ *vs.* time (Table-1, Fig. 1). To ascertain the reaction rate dependence and the order of reaction on [Substrate] the reactions are carried out at different concentrations of propanone thiosemicarbazone (PTSC). The reaction rate increased progressively with increase in [substrate] (Table-1). When log k_1 is plotted against log [PTSC], a straight line with fractional slope (*ca.* 0.43) is obtained.

TABLE-1
DEPENDENCE OF RATE ON THE CONCENTRATION OF CAT AND PROPANONE THIOSEMICARBAZONE (PTSC) AT 293K.

10^3 [CAT] M	10^2 [PTSC] M	[$HClO_4$] M	% AcOH (v/v)	10^4 (s^{-1}) k_{obs}
1.136	3.811	0.3	30	4.401
1.420	3.811	0.3	30	4.606
1.704	3.811	0.3	30	4.515
1.420	2.668	0.3	30	3.944
1.420	4.954	0.3	30	5.117
1.420	6.098	0.3	30	5.629
1.420	7.241	0.3	30	6.031
1.420	3.811	0.3	30	5.166
1.420	3.811	0.3	40	5.597
1.420	3.811	0.3	45	6.348
1.420	3.811	0.3	50	6.854

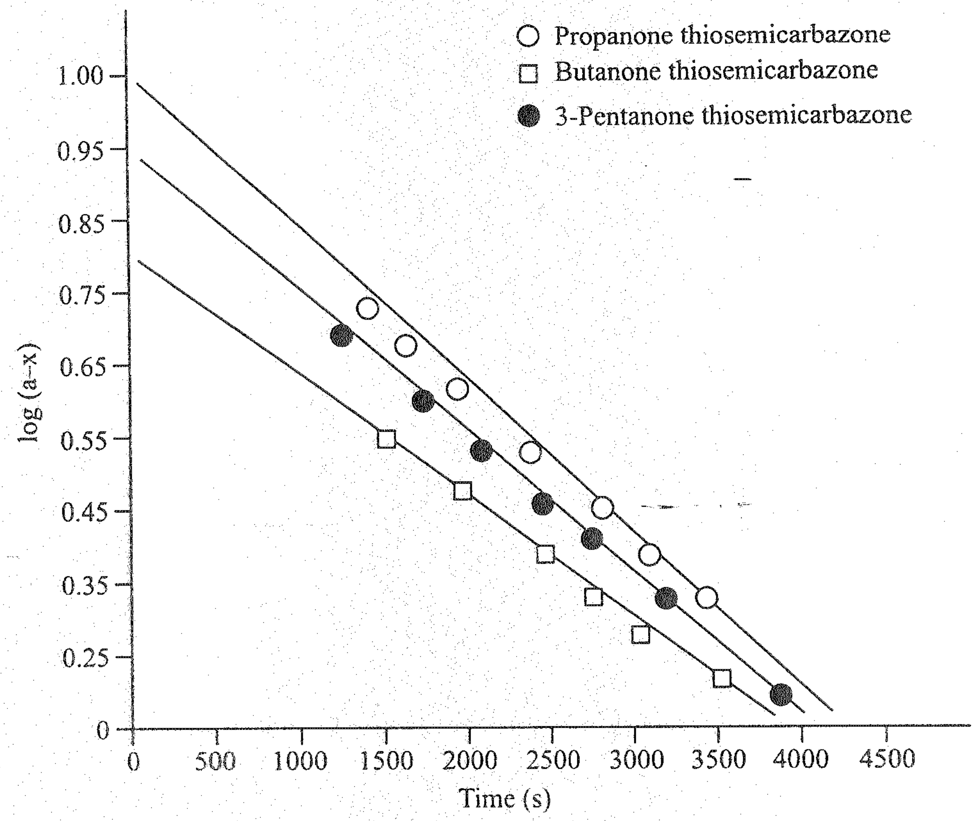


Fig. 1 Dependence of rate on concentration of CAT: plot of log (a – x) *vs.* Time

Rate constant values decrease linearly with increase in $[H_3O^+]$. When log $(1/k_1)$ is plotted against $[H_3O^+]$, a straight line with slope less than unity (*ca.* 0.61) (Fig. 2) is obtained indicating that the reaction has inverse fractional order dependence on $[H_3O^+]$ (Table-2).

The rate of oxidation increases with increase in acetic acid content of the reaction mixture. Thus the decrease in solvent polarity enhances the reaction rate

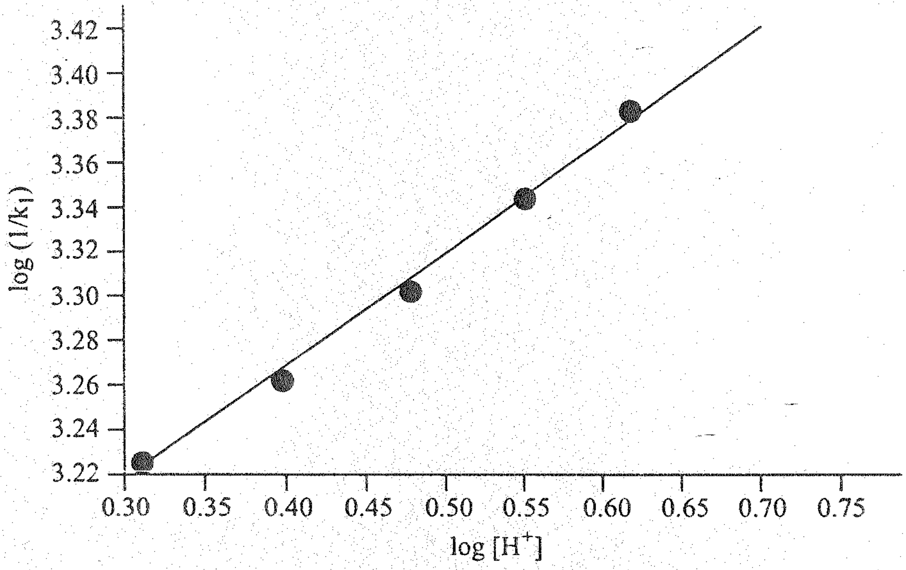


Fig. 2 Dependence of rate on concentration of the $HClO_4$

(Table-1). A plot of log k_1 *vs.* $(D - 1)/(2D + 1)$ gave a straight line[10], where D is the dielectric constant of the medium indicating the interaction between two dipoles or an ion and a dipole in the rate limiting step. The reaction is not that much susceptible to ionic strength variations of the medium (Table-2).

TABLE-2
COMPARISON OF RECALCULATED VALUES AND EXPERIMENTAL RATE CONSTANTS FOR OXIDATION OF PROPANONE THIOSEMICARBAZONE

[PTSC] × 10^2 M	[$HClO_4$] M	[$NaClO_4$] M	10^4 (Expt.)	k_{obs} (s^{-1}) (Recalcd.)
2.668	0.30	0	3.944	3.772
3.811	0.30	0	4.606	4.576
4.954	0.30	0	5.117	5.170
6.098	0.30	0	5.629	5.620
7.241	0.30	0	6.031	5.982
3.811	0.20	0.35	6.141	6.050
3.811	0.25	0.30	5.373	5.409
3.811	0.30	0.25	4.833	4.892
3.811	0.35	0.20	4.386	4.464
3.811	0.40	0.15	4.051	4.106

[CAT] = 1.420 × 10^{-3}; Temp. = 293K; [solvent] = 30% AcOH – 70% H_2O (v/v).

Addition of *p*-toluene sulphonamide, the reduced product of oxidant, in the range 2.92 × 10^{-3} M to 5.84 × 10^{-3} M has no effect on the reaction rate. The reaction mixture fails to induce the polymerization of acrylamide ruling out the possibility of free radicals as intermediates during the course of the reaction. The values of various thermodynamic parameters have been evaluated from the measurements of rates of the reactions at various temperatures for all the substrates (Table-3, Fig. 3).

TABLE-3
VARIOUS THERMODYNAMIC PARAMETERS

Substrate	$10^4 k_1 (s^{-1})$				$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)
	288 K	293 K	298 K	303 K			
(1)	3.838	4.606	5.413	6.333	22.40	–119.83	57.51
(2)	4.040	4.825	5.609	6.601	20.63	–121.75	56.30
(3)	4.149	4.975	5.757	6.781	20.94	–123.57	57.14

[CAT] = 1.420 × 10^{-3} M; [$HClO_4$] = 0.3 M; [solvent] = 30% AcOH – 70% H_2O (v/v).

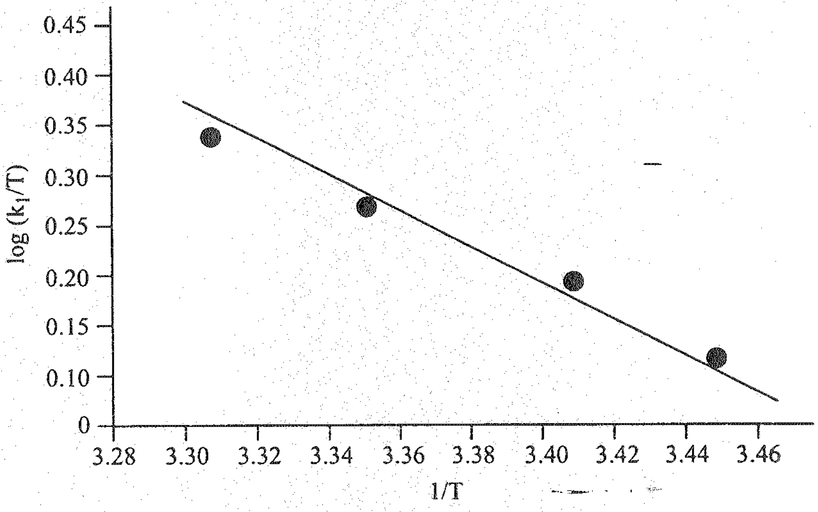


Fig. 3 Dependence of rate on temperature: Plot of log (k_1/T) *vs.* 1/T

Mechanism

CAT furnishes different types of reactive species in aqueous and partial aqueous solutions[11].Under the present experimental conditions (0.3 M $HClO_4$) the possible oxidising species may be $ArSO_2NH_2Cl^+$ ($CATH^+$) and H_2OCl^+. On the basis of the observed results in the present study (effect of added *p*-toluene sulphonamide), $ArSO_2NH_2Cl^+$ is proposed as the actual reacting species.

The essential reaction sequences involved in the reaction may be represented as

$$CATH^+ + S \overset{K_1}{\rightleftharpoons} \text{Complex (Y)} + H^+$$

$$Y \xrightarrow[\text{Slow}]{k_s} \text{Products}$$

where S is substrate.

This mechanism leads to the rate law,

$$\frac{1}{k_{obs}} = \frac{[H^+]}{k_s K_1 [S]} + \frac{1}{k_s}$$

As expected from the rate law, the plots of $1/k_{obs}$ *vs.* $[H^+]$ and $1/k_{obs}$ *vs.* 1/[S] are linear. The plot of $1/k_{obs}$ *vs.* 1/[S] has an intercept on the axis confirming the mechanism proposed. The reactivity of substrates towards the oxidant is in the order: (3) > (2) > (1). The trend in reactivity of these substrates can be understood from the fact that as the size of the alkyl group increases, its electron donating ability increases.

The fairly constant values of $\Delta H^{\neq}$ lend support to the fact that similar mechanism operates in each of these cases. The reaction has negative entropy of activation, indicating more orderliness of the transition state than the initial state.

The recalculated and experimental rate constants are reasonably in good agreement (Table-3), thus confirming the mechanism proposed and the rate law derived.

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