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Mechanistic Investigations on Reactivities of Alkanone Semicarbazones towards Chloramine-T: A Kinetic Study

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Kinetics of oxidation of few alkanone semicarbazones by chloramine-T in aqueous acetic acid medium has been investigated in the presence of perchloric acid at 308 K. The reaction follows first order kinetics in [CAT], fractional order in [substrate], inverse fractional order in [H_3O^+]. Variation in ionic strength of the medium and addition of the reaction product, *p*-toluene sulphonamide has no effect on the rate of reaction. An increase in the rate is observed when the dielectric constant of the medium is decreased. The stoichiometries of the reactions are established, the oxidation products are identified and the relative reactivities of the various substrates have been determined. The rate limiting step has been identified, the rate coefficients of these steps and the related activation parameters have also been evaluated. The validity of the deduced rate law has been checked by recalculating the rate constants.

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

INTRODUCTION

Chloramine-T (CAT), an organic N-halogeno-N-metallo reagent and a source of positive chlorine has been used for oxidation of alcohols[1–4], amino acids[5], aldehydes and ketones[5] in both acidic and alkaline media. CAT interacts with a wide range of functional groups both as a chlorinating agent and an oxidizing agent in aqueous and partially aqueous media in the presence of acids or alkalis.

The present work is an attempt to investigate the oxidation mechanism of some alkanone semicarbazones by chloramine-T in aqueous acetic acid [25%(v/v)] in the presence of perchloric acid and to study their relative reactivities.

EXPERIMENTAL

Chloramine-T (E. Merck, GR) is purified by the method of Morris *et al.*[6] Semicarbazide hydrochloride (EQ. Qualigens) is used after recrystallization. Semicarbazones of propanone (PSC), butanone (BSC) and 3-pentanone (DEKSC) are prepared by reported procedure.

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All the kinetic runs are carried out in a thermostat, maintaining pseudo first order conditions by keeping substrate concentration always in large excess (nearly 10 folds) over that of oxidant concentration. To forestall any interference from photocatalysis the reactions are carried out in darkened flasks. The reactions were initiated by the rapid addition of known quantities of CAT solutions, thermally equilibrated at a desired temperature, to mixtures of appropriate amounts of alkanone semicarbazone, acetic acid and $HClO_4$ pre-equilibrated at the same temperature. The progress of the reaction is monitored by iodometric estimation of unreacted oxidant at regular intervals of time. The rates are followed for at least two half-lives. The ionic strength of the medium is maintained using sodium perchlorate.

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 303 K for 24 h. The observed stoichiometries may be represented by the equation

$$>C{=}N{-}NHCONH_2 + 2ArSO_2NHCl + 2H_2O \longrightarrow$$

$$>C{=}O + 2ArSO_2NH_2 + N_2 + CO_2 + NH_4^+ + H^+ + 2Cl^-$$

The products of the oxidations are identified by the standard tests.

RESULTS AND DISCUSSION

To determine the dependence of the reaction rate on [CAT] and consequently the order, the reaction is carried out at different concentrations of CAT by keeping the concentrations of other reactants constant. The reaction has first order dependence (Fig. 1) at all the concentrations of CAT. The results are enlisted in Table-1.

TABLE-1
DEPENDENCE OF RATE ON THE CONCENTRATION OF CAT AND PROPANONE SEMICARBAZONE

S.No.	[CAT] × 10^4 M	[PSC] × 10^3 M	$10^5 k_1$ (s^{-1})
1.	12.43	52.11	31.83
2.	14.91	52.11	32.90
3.	17.39	52.11	30.70
4.	12.43	39.08	29.47
5.	12.43	65.14	34.89
6.	12.43	78.17	37.14
7.	12.43	91.19	38.97

[Solvent] = 25% AcOH–75% H_2O (v/v), [$HClO_4$] = 1 M, Temperature = 308 K

To ascertain the reaction rate dependence and the order of reaction on [substrate] the reactions are carried out at different concentrations. The results

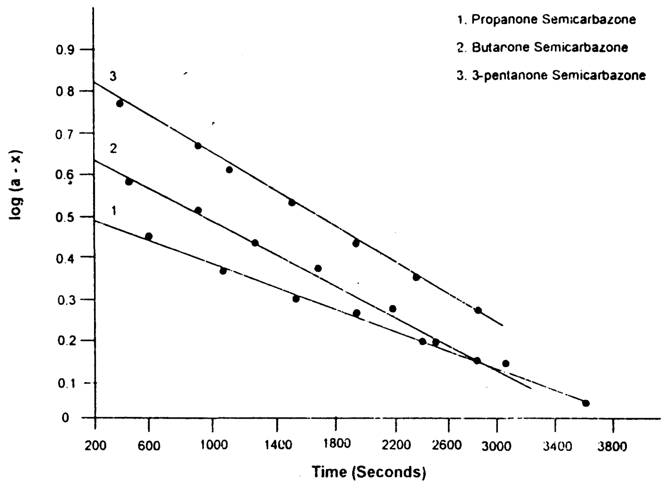

Fig. 1. Dependence of rate on the concentration of CAT: plot of log (a – x) *vs.* time

recorded in Table-1 indicate that the rate when [substrate] is varied at constant [CAT] and [H_2O^+] increased progressively with increase in [substrate]. The plot of log k_1, against log [PSC] is a straight line with fractional slope (Fig. 2). Thus

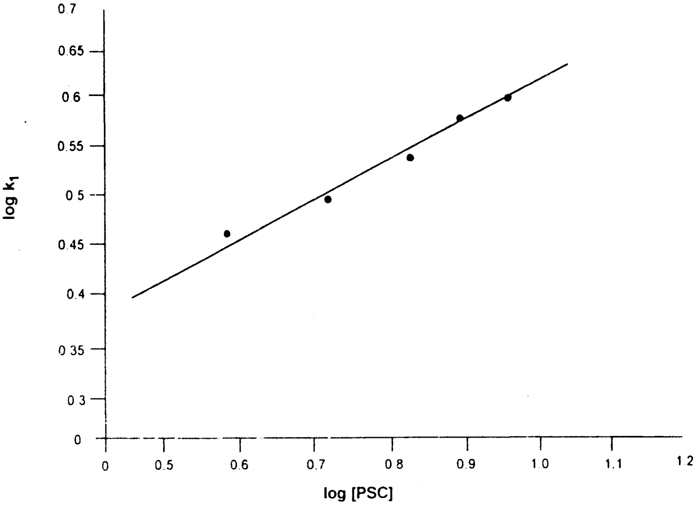

Fig. 2. Dependence of rate on the concentration of propanone semicarbazone: plot of log k_1 *vs.* log [PSC]

the reaction has fractional order dependence on [substrate].

At constant [CAT] and [PSC] the rates decreased with increase in [$HClO_4$]. The results are reported in Table-2. Plots of log $1/k_1$ Vs log [H_2O^+] is linear with slope less than unity (Fig. 3).

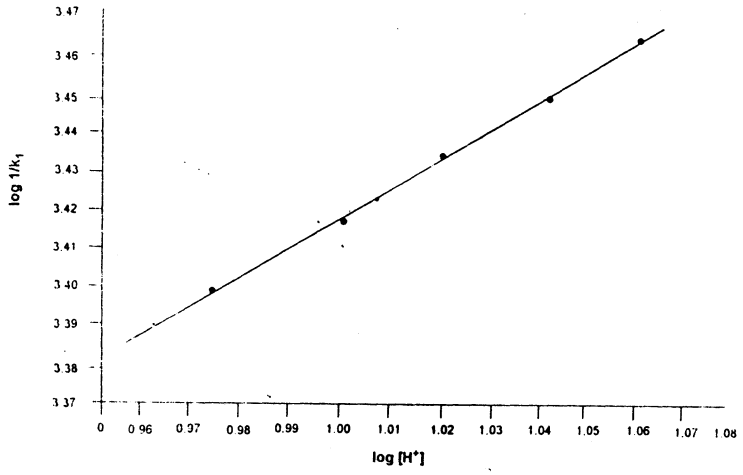

Fig. 3. Dependence of rate on the concentration of $HClO_4$: plot of log $1/k_1$ *vs.* log $[H^+]$.

TABLE-2
DEPENDENCE OF RATE ON THE CONCENTRATION OF PERCHLORIC ACID AND SODIUM PERCHLORATE

S.No.	$[HClO_4]$ M	$[NaClO_4]$ M	$10^5 k_1$ (s^{-1})
1.	0.95	0.25	39.91
2.	1.00	0.20	38.38
3.	1.05	0.15	36.94
4.	1.10	0.10	35.50
5.	1.15	0.05	34.30
6.	1.00	0.10	39.50
7.	1.00	0.30	37.68
8.	1.00	0.40	38.09

[CAT] = 12.43×10^{-4} M; [PSC] = 52.11×10^{-3} M, [Solvent] = 25% ACOH–75% H_2O (v/v)

The rate of oxidation increases with increase in acetic acid content of the medium (Table-3). The plot of log k_1 *vs.* (D-1/2D+1) gave a straight line[7] indicating that in the rate determining step of the reaction there is an interaction between two dipoles or an ion and a dipole.

TABLE-3
DEPENDENCE OF RATE ON DIELECTRIC CONSTANT OF THE MEDIUM

% AcOH–% H_2O	$10^5 k_1$ (s^{-1})
25.0–75.0	31.83
30.0–70.0	34.67
35.0–65.0	38.71
40.0–60.0	41.95

[CAT] = 12.43×10^{-4} M; [PSC] = 52.11×10^{-3} M; $HClO_4$ = 1 M; Temperature = 308 K

The reaction is not that much susceptible to ionic strength variations of the medium (Table-2). Addition of *p*-toluene sulphonamide (PTS) the reduced product of oxidant, in the range 2.92×10^{-3} to 5.40×10^{-3} M has no effect on the reaction rate.

Free radicals as intermediates during the course of the reaction are ruled out since the reaction mixture failed to induce polymerisation of added acrylamide. The rates are measured at different temperatures and the activation parameters are computed from the Eyring plot (Table-4, Fig. 4 for propanone semicarbazone). From the slope and intercept the enthalpy of activation ($\Delta H^{\#}$) and entropy of activation($\Delta S^{\#}$) are calculated.

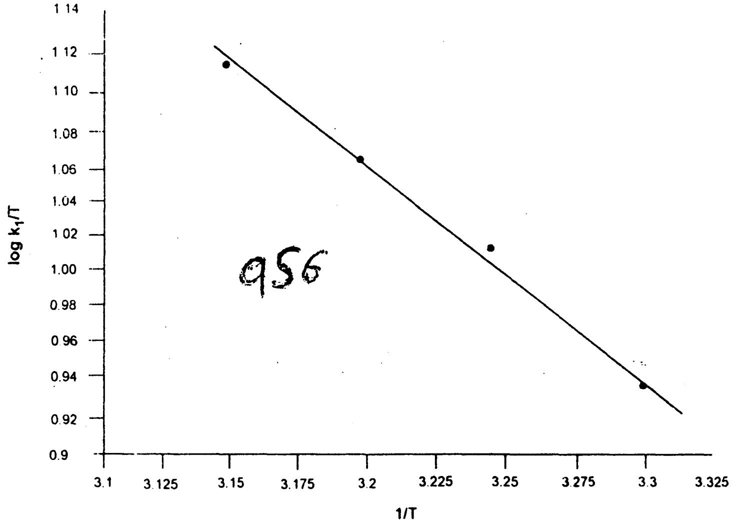

Fig. 4. Dependence of rate on temperature: plot of log k_1/T *vs.* 1/T

TABLE-4
VARIOUS THERMODYNAMIC PARAMETHERS

Substrate	$10^5 k_1$ (s^{-1}) Temp. (K) 303	308	313	318	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
PSC	25.93	31.83	36.63	41.34	23.45	−105.47	−9.034
BSC	28.86	33.85	41.26	46.06	23.93	−102.79	−7.729
DEKSC	32.06	36.18	44.93	50.66	22.97	−100.68	−8.039

[CAT] = 12.43×10^{-4} M; Solvent = 25% AcOH–75% H_2O (v/v); [$HClO_4$] = 1 M

The observed negative entropy of activation indicates that transition state of the rate-limiting step is more ordered than the initial state. Effects of structural variation have been investigated under identical conditions and the rate constants are given in Table-5.

TABLE-5
EFFECT OF STRUCTURAL VARIATION ON THE RATE OF THE REACTION

S.No.	Substrate	10^3 [Substrate] M	10^5 k_1 (s^{-1})
1.	PSC	52.11	31.83
2.	BSC	46.45	33.85
3.	DEKSC	42.19	36.18

[CAT] = 12.43×10^{-4} M; Solvent = 25% AcOH–75% H_2O (v/v); [$HClO_4$] = 1 M;
Temp. = 308 K

CAT is fairly a strong electrolyte[8–10] in aqueous solutions. It furnishes different types of reactive species in aqueous and partial aqueous solutions depending upon the pH of the medium. Under the present experimental conditions the possible oxidising species may be $ArSO_2NH_2Cl^+$ and H_2OCl^+ if H_2OCl^+ is the active species; retardation of rate by the added *p*-toluene sulphonamide could be expected because of the following equlibria:

$$ArSO_2NH_2Cl^+ + H_2O \rightleftharpoons ArSO_2NH_2 + H_2OCl^+$$

But no such effect is observed in this reaction. This rules out H_2OCl^+ as the possible oxidising species. Hence in the present investigation $ArSO_2{\cdot}NH_2Cl^+$ is assumed to be the reactive species.

Mechanism of oxidation

The essential reaction sequences involved are:

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

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

where 'S' is the substrate.

The mechanism leads to the rate law as

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

The rate law predicts that a plot $1/k_{obs}$ Vs $1/[S]$ at constant $[H^+]$ and a plot of $1/k_{obs}$ *vs.* $[H^+]$ at constant [S] should be linear. This has been observed. Further the double reciprocal plot of $1/k_{obs}$ *vs.* $1/[S]$ at constant $[H^+]$ has an intercept on rate axis showing the intermediate formation of a complex.

The constants K_1 and k_s computed from the plots of $1/k_{obs}$ *vs.* $1/[S]$ and $1/k_{obs}$ *vs.* $[H^+]$ were used to recalculate the rate constants from the above rate law. The recalculated values and experimental constants are reasonably in good agreement (Table-6) confirming the mechanism proposed and the rate law derived.

TABLE-6

COMPARISON OF RECALCULATED AND EXPERIMENTAL RATE CONSTANTS FOR OXIDATION OF ALKANONE SEMICARBAZONES BY CHLORAMINE-T IN AQUO-ACETIC ACID [25% (v/v)] MEDIUM IN PRESENCE OF PERCHLORIC ACID AT 308 K

S.No.	[PSC] × 10^3 M	[$HClO_4$] M	[$NaClO_4$] M	10^5 k_I (s^{-1})	
				Expt.	Recalcd.
1.	39.08	1.00	0	29.48	29.37
2.	52.11	1.00	0	31.83	32.58
3.	65.14	1.00	0	34.89	34.87
4.	78.17	1.00	0	37.15	36.59
5.	91.19	1.00	0	38.97	37.93
6.	52.11	0.95	0.25	39.91	38.21
7.	52.11	1.00	0.20	38.83	36.87
8.	52.11	1.05	0.15	36.98	35.61
9.	52.11	1.10	0.10	35.50	34.44
10.	52.11	1.15	0.05	34.30	33.34

[CAT] = 12.43 × 10^{-4} M; Temperature = 308 K

The reactivity of substrates used towards the oxidant is in the order: DEKSC > BSC > PSC. The observed trends may be understood by utilizing the electron releasing inductive effect of alkyl groups, namely, as the size of alkyl group increases its electron donating ability increases.

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REFERENCES

1. S.P. Mushran, R.N. Mehrotra and R. Sanchi, *J. Indian Chem. Soc.*, **51,** 594 (1974).
2. A. Kumar, R.M. Mehrotra and S.P. Mushran, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **24,** 181 (1976).
3. D.S. Mahadevappa and H.M.K. Naidu, *Indian J. Chem.*, **14A**, 808 (1976).
4. V. Venkateswaran and K. Selvaraj, *Indian J. Chem.*, **36A**, 328 (1997).
5. ———, *Indian J. Chem.*, **40B**, 101 (2001).
6. J.C. Morris, J.A. Salazar and W.A. Winman, *J. Am. Chem. Soc.*, **70**, 2036 (1948).
7. T. Veeraiah and S. Sondu, *J. Indian Chem. Soc.*, **74**, 402 (1997).
8. A.R.V. Murthy and V.S. Rao, *Proc. Indian Acad. Sci.*, **35A**, 69 (1952).
9. M.C. Agarwal and S.P. Mushran, *Z. Naturforsch*, **27B,** 401 (1972).
10. E. Bishop and V.J. Jennings, *Talanta*, **1**, 197 (1958); M.M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978).

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