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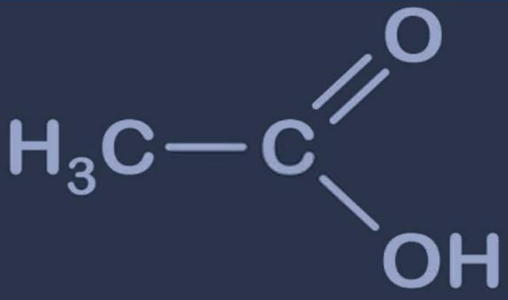

DR. P. PARIMALA DEVI

MECHANISTIC INVESTIGATION OF OXIDATION OF ALIPHATIC KETONE SEMICARBAZONES BY CHLORAMINE-T IN AQUEOUS ACETIC ACID MEDIUM

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PREFACE

Chloramine-T (CAT), the sodium salt of N-chloro-p-toluenesulphonamide, is a low-cost mild oxidizing agent with a wide range of uses. Most importantly, it can be used in acidic, neutral, and basic conditions. As a result, it has been widely used in chemistry, particularly in organic synthesis and analytical chemistry. Chloramine-T acts as a source of halonium cation and nitrogen anion and thus acts as base and nucleophile. It reacts with a wide range of functional groups and carries different molecular transformations.

This book focuses on the studies of kinetics of oxidation of some aliphatic ketone semicarbazones by chloramine –T and also has been investigated with a view to propose suitable mechanism, rate law and correlate the reactivity of various substrates with their structures.

Acknowledgement

First and foremost, I owe it all to **Almighty God** for granting me the wisdom, health, strength and nice environment to undertake this work task and enabling me to its successful completion of this work.

I would like to thank the Management, Principal and Dean of our college for their encouragement and support to complete this work.

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Dr. P. Parimala Devi

INDEX

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Chapter 1

Introduction

N-halo oxidants a potential source of positive halogen ions in aqueous acetic acid solutions, have been widely used as effective oxidants and halogenating agents for a wide variety of organic compounds. Their halogenating and oxidizing capabilities are well documented. Among the various N-halo oxidants, Chloramine – T(CAT) has been used as oxidant and as well as chlorinating agent for a variety of organic substrates. A fairly detailed survey of the literature reveals that mechanistic aspects of the reactions of semicarbazones have not been tried by exploiting the kinetic study as a tool.

The literature review also indicate that chloramine-T has not been tried on the semicarbazones of aliphatic ketones particularly to study how the rate changes when the alkyl groups attached to the carbonyl group is varied. Hence it was thought worthwhile to investigate the oxidation of few aliphatic ketone semicarbazones using CAT as an oxidizing agent.

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

Oxidation, a process commonly observed in day – to daily life[1], is one among the extensively studied chemical reactions. This is evident from the accumulation of a large number of empirical data and conclusions available.

A study of oxidation reactions has been a subject of major importance to many chemists and the elucidation of the mechanism is undoubtedly one of the most fascinating problems in chemistry. In this direction, the studies of kinetics of various reactions play an important role.

N-halo compounds because of the capability to act as source of halonium ion in solutions, ready availability and ease of handling proved themselves as effective oxidants and halogenating agents for a wide variety of organic compounds. They are even more preferred over molecular halogen themselves. Their diverse nature is well documented in literature[2-7].

Their use for the quantitative estimations of organic compound has also been reported[8-10]. Examples of such N – halogen substituted oxidants are N – bromosuccinimide[11], N-chlorosuccinimide[12,13], N – chloro – 3 – methyl – 2,6 – diphenyl 1,4- piperidinone[14,15], N –bromosaccharin[16], N – chlorosaccharin[17], N-chloro-N-sodio-p-toluenesulphonamide[18,19], N-bromo-N-sodio-p-toluenesulphonamide[20], dichloramine-T[21], dichloramine-B[22], iodamine-T[23], N – chloro – N – sodio-p-chlorobenezenseulphonamide[24], N-chloro-p-methylbenzamide[25], N-chloro-p-chlorobenzamide[25], N-chloro-p-nitrobenzamide[25], etc.

Studies with Chloramine – T (CAT):

Chloramine- T, the N-chloro-N-sodio-p-toluenesulphonamide has been used as a resource of positive chlorine in wide variety of reactions. Excellent reviews are available on the reactions of CAT[19,26-29]. CAT and other related N-halogeno-N-metallo aryl sulphonamides exhibit unique dual behavior as they act as a source of both halonium cation and nitrogen anion. Compounds are most commonly represented as,

$R\ C_6H_4SO_2N^-X\ M^+$ $R\ C_6H_4SO_2^-NX\ M^+$

I **II**

For Chloramine – T, $R = CH_3$; X = Cl; M = Na

In general, these sulphonamide derivatives are stable in aqueous solutions. They behave as strong electrolytes and strong oxidants in both acidic and alkaline media (CAT, E_{red} = 1.138 V at p^H 0.65 and 0.5V at p^H 12).[30,31]

CAT has been used for the oxidation of primary alcohols[32,] Secondary alcohol[33], alicyclic alcohols[34], allyl alcohol[35], cinnamyl alcohol[36], heterocyclic alcohol[37], glycine and aspartic acid [38], p- substituted phenyl methyl sulphoxides[39], glutamic acid [40], aldehydes and ketones [18,41-43] in acidic media.CAT also has been used to oxidise various substrates in neutral and alkaline medium[44-46].

It has been well established that CAT is sTable in strongly aqueous acidic medium for more than 48 hours[47] and its sTable characteristics have been reviewed by several authors.[30,48]

Studies on the Oxidation of Semicarbazide and Semicarbazones:

Jovanovic, Slobodanka et al[49]., studied kinetics and mechanism of the synthesis of 5-nitro-2-furaldehyde semicarbazone in water or in DMF. Kinetics of the reaction of dicarboxylic acid anhydrides with the derivatives of semicarbazide $Ph\text{-}NH\text{-}CO\text{-}NR\text{-}NH_2$ where R=H, $CH_2\text{-}CH_2\text{-}OH$, in dimethyl formamide (DMF) was examined by Shevchenko et al., [50] Polarographic studies on kinetics of formation of furfural semicarbazone in HCl medium has also been reported [51].

Kinetic studies on the oxidation of semicarbazide by iodamine-T, iodine monochloride and iodine in the presence of perchloric acid in aqueous acetic acid medium has been studied[52].

The reactions followed zero order kinetics in the substrate, first order in the oxidants and fractional order in H^+ with all the oxidants.

The rates decreased slightly with increase in ionic strength of the medium in IAT and ICl oxidations, while the reverse trend was observed with I_2.

Decrease in dielectric constant of the medium increased the rates with IAT and ICl, while it decreased the rate in I_2 oxidations. Addition of the reduced product, p-toluenesulphonamide had no effect on the rate with IAT.

Addition of I^- had slight negative and positive effects on the rates of oxidations with IAT and ICl respectively, but the negative effect was considerable in I_2 oxidations. Mechanisms consistent with the observed rate laws have been proposed and discussed.

Rate determining steps have been identified and their coefficients calculated. As a representative example, mechanism proposed and the rate law derived for the oxidation with iodamine-T is shown in Scheme-1.

$$\mathrm{RNHI + H^+ \rightarrow RNH_2I^+} \qquad \text{(Fast)}$$

$$\mathrm{RNH_2I^+ + H_2O \rightarrow H_2OI^+ + RNH_2} \qquad \text{(Slow,r.d.s)}$$

$$\mathrm{H_2OI^+ + S \rightarrow S' + H_3O^+} \qquad \text{(Fast)}$$

$$\mathrm{S' + H_2OI^+ \rightarrow Products} \qquad \text{(Fast)}$$

Scheme-1

Scheme-1 leads to the following rate law,

$$-d[IAT] / dt \quad = \quad K_1k_2[RNHI]_0 [H^+] [H_2O]/ 1+ K_1[H^+]$$

B. Thimme Gowda and Ishwara Bhat[53] studied the kinetics and mechanism of oxidation of semicarbazide by Chloramine –B(CAB), Bromine –B(BAB) and Dichloramine –B(DCB) in 50%(v/v) aqueous methanol medium.

Oxidations by CAB and DCB show first order dependence in [oxidant], fractional order in [SC], and fractional order in $[H^+]$.

In case of BAB oxidants in acid medium the reaction orders in [BAB] and [SC] are unity and fractional, but inverse fractional in $[H^+]$. In alkaline medium the oxidation in first order in [BAB] and zero order each in [SC] and $[OH^-]$.

Variations in ionic strength and dielectric constant of the reaction medium and added reaction products do not have any significant effect on the rates of oxidants.

To account for the observed facts the following mechanisms and rate laws have been proposed.

i. With chloramine –B (CAB) and Dichloramine –B (DCB):

$$RNHCl + H^+ \rightarrow H_2OI^+ + RNH_2 \quad \text{(fast)}$$

$$RNH_2Cl^+ + S \rightarrow Y \qquad \text{(fast)}$$

$$\mathrm{Y} \rightarrow \mathrm{Y' + RNH_3^+} \qquad \text{(Slow)}$$

$$\mathrm{Y' + RNH_2Cl^+} \rightarrow \text{Products} \qquad \text{(Fast)}$$

Scheme-2

Based on scheme -2, the following rate law has been deduced.

$$-d[\mathrm{CAB}] / dt \quad = \quad K_1\, K_2 k_3[\mathrm{CAB}]_t\, [\mathrm{S}][\mathrm{H}^+]/ 1+ K_1[\mathrm{H}^+] + K_1\, K_2[\mathrm{H}^+]\, [\mathrm{S}]$$

ii. With Bromamine –B:

a. In acid medium:

$$\text{b. } \mathrm{SH^+} \xrightleftharpoons{K_6} \mathrm{S + H^+} \qquad \text{(fast)}$$

$$\text{c. } \mathrm{RNHBr + S} \xrightleftharpoons{K_6} \mathrm{Z} \qquad \text{(fast)}$$

$$\text{d. } \mathrm{Z} \xrightarrow{k_7} \mathrm{Z' + RNH} \qquad \text{(slow)}$$

$$\text{e. } \mathrm{Z' + RNHBr} \xrightarrow{k_8} \text{Product} \qquad \text{(fast)}$$

Scheme-3

Based on scheme-3, the following rate law has been deduced.

$$-d[\mathrm{BAB}]/dt = K_6\, k_7\, [\mathrm{RNHBr}]_0\, [\mathrm{S}]/ 1+ K_6\, [\mathrm{S}]$$

In alkaline medium:

$$\text{a. } \mathrm{RNBr + H_2O} \xrightarrow{\boxed{k_9}} \mathrm{RNH_2 + OBr^-} \qquad \text{(slow)}$$

$$\text{b. } \mathrm{OBr^- + S} \xrightarrow{k_{10}} \text{Product} \qquad \text{(fast)}$$

Scheme-4

The following rate law has been deduced based on scheme-4, -d[BAB]/dt = k_9 [BAB] [H_2O] Oxidations of semicarbazones of acetone, ethyl methyl ketone, acetophenone and 4'- methyl acetophenone by Thallium [III] in aqueous acid containing H_2SO_4 and Cl^- was examined[54]. The rate of oxidation decreased with increasing [H^+], with decreasing percentage of acetic acid and with increasing [Cl^-].

The product was the corresponding carbonyl compound. Induced polymerisation was not observed when acrylamide was added, suggesting that no free radicals are involved in the reaction. Activation parameters were calculated.

Kinetics of oxidation of semicarbazide by CAT in aqueous perchloric acid medium and DCT in 1:1 (v/v) aqueous methanol medium was studied by B. Thimme Gowda and B. S Sherigara[55].Rate laws for oxidation of semicarbazide by CAT and DCT are given. Effects of addition of reaction product and variations in ionic strength and dielectric constant of the medium were also investigated. Mechanisms in accordance with the observed rate laws are discussed. Thermal decomposition kinetics of Nickel fluorenone semicarbazone was reported by S. Laly; Parameswaran, Geetha[56].

Oxidation of semicarbazide, thiosemicarbazide, carbohydrazide, thiocarbohydrazide, thiocyanate, thiourea and the derivatives with aqueous cobaltic ions in acid media was studied by S. D. Ravi Prakash, B. S. Sherigara et al., SuiTable mechanism consistent with the observed results have been proposed.

K. Meenal and T.S.J. Bai[58] report the kinetic studies of the oxidation of acetophenone semicarbazone, p- methoxy acetophenone semicarbazone by peroxodisulphate.

B.V. Mohankumar et al [59]., studied the oxidation of semicarbazide, thiosemicarbazide and their derivatives by potassium trifluoro (oxalato) manganate (III). The reactions have been followed titrimetrically and also potentiometrically in some cases. The stoichiometries of the reactions are established and the oxidation products identified.

Kinetics and mechanism of oxidation of iron (II) by N-chloro-p- substituted benzenesulphonamides has been reported[24].

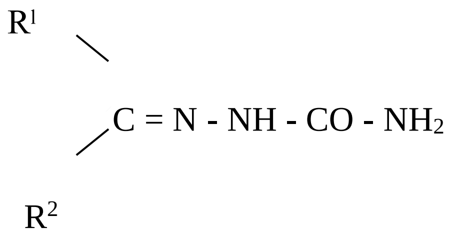
Abdol Reza Hajipour and Shadpour.E. Mallakpour et al [60]., report the conversion of semicarbazones, oximes, phenylhydrazones and 2,4-dinitrophenyldrazones to carbonyl compounds with benzyl triphenylphosphoniumchlorochromate (BTPPCC) in the presence of aluminium chloride under non- aqueous conditions.

Chapter 2

Experimental Methodology

(a) Materials:

The following ketone semicarbazones (1) - (3) were prepared by following published procedure [61].



$$\mathrm{R^1R^2C=N-NH-CO-NH_2}$$

Compound	R^1	R^2
(1)	CH_3	CH_3
(2)	CH_3	CH_2CH_3
(3)	CH_2CH_3	CH_2CH_3

The compounds were purified by repeated crystallization to constant melting point.

The samples were dried in vacuum at a suitable temperature just before the kinetic runs. Melting points reported were determined using HECO melting point apparatus and are uncorrected.

General Procedure for the Preparation of Aliphatic Ketone Semicarbazones: Semicarbazones used in this study were prepared by following the reported method[61]. To a hot solution containing semicarbazide hydrochloride (0.1M) and sodium acetate (0.1M), the aliphatic ketone (0.1M) is added in drops. The mixture is shaken well and refluxed over a boiling water bath for about an hour. On cooling crystals of aliphatic ketone semicarbazones get separated. The product obtained was collected and recrystallised from ethanol.

Propanonesemicarbazone (1):

Propanone (7.1 ml) is added to a hot solution of semicarbazide hydrochloride (11.2gms) and sodium acetate (13.6 gms). The mixture is shaken and refluxed for an hour. The colourless crystals obtained on cooling were purified by recrystallisation from ethanol. Yield 90%, m.pt.189 - 191^{o} C.

Butanone Semicarbazone (2):

Treatment of butanone (9.0 ml) with semicarbazide hydrochloride (11.2 gms) and sodium acetate (13.6 gms) under reflux conditions gave (2). It is recrystallised from ethanol. Yield 94%, m.pt. 146-148°C.

3-Pentanone Semicarbazone (3):

3-Pentanone (10.1 ml) when added with stirring under reflux conditions into a solution of semicarbazide hydrochloride (11.2 gms) and sodium acetate (13.6 gms) yield 3 - pentanonesemicarbazone. The product obtained in 90% yield when recrystallised from ethanol melted at 210-211°C.

Oxidant: Chlormine - T (CAT) (GR, E. Merck), was purified by the method of Morris et a1[62].,

Semicarbazide hydrochloride: Semicarbazide hydrochloride (EQ. Qualigens) was used as such.

Sodium acetate: Sodium acetate (EQ. Qualigens) was used.

Acetic Acid: Acetic acid (EQ. Qualigens) was refluxed with chromium trioxide for five hours with the addition of acetic anhydride corresponding to the water content of the acid. The solid that separated was filtered off and the acid was distilled from an all-glass apparatus. Large head and tail fractions were rejected and the fraction distilling at 391K was collected. The distillate was protected from atmospheric moisture.

Perchloric Acid: Perchloric acid (EQ. Qualigens) was used as such. Sodium perchlorate and other chemicals used were all of excellar grade. Doubly distilled water is used to prepare solutions.

(B) Methods:

Kinetic Runs: All the kinetic runs were carried out in a thermostat with an accuracy of ± 0.2 °C, maintaining pseudo first order conditions, by keeping substrate concentration always in large excess (nearly 10 folds) over that of oxidant concentration. Sodium per chlorate was used to keep the ionic strength of the medium constant. To forestall any interference from photo catalysis the reactions were carried out in darkened flasks. Solutions of the substrate and oxidant were pre-equilibrated in a thermostat at the desired temperature for an hour before mixing. The reaction was started by pipetting out a known volume of the oxidant solution on to the substrate solution in a stoppered conical flask. The rate was followed by withdrawing aliquots (2 ml) of the reaction mixture at various intervals of time, adding to known excess of potassium iodide solution (5%), treating it with a known excess of sodium thiosulphate and titrating the unreacted thiosulphate against a standard iodine solution using starch as indicator. The rates were followed for atleast two half - lives. The results were reproducible within ± 3%.

(C) Calculations:

Rate Constants:

The pseudo first order rate constants with respect to the oxidant was computed using the first order integrated rate equation

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

With the identities $a = (V_\infty - V_0)$ and $(a - x) = (V_\infty - V_t)$. When log (a - x) was plotted against time 't' a straight line was obtained, from the slope of which, the pseudo first order rate constant k_1 was determined. ($k_1 = \text{slope} \times 2.303$). The k_1 values are reported in s^{-1}.

Activation Parameters:

Depending upon the reaction conditions, the reactions were carried out at various temperatures. According to the theory of absolute reaction rates[63], the following expression holds good for the rate constant of a reaction in solution.

$$k_1 = (kT/h)\, e^{\Delta S\# / R}\, e\text{-}^{\Delta H\# / RT}$$

where k_1 is the rate constant of the reaction, $\Delta H^{\#}$ - enthalpy of activation, $\Delta S\#$ - entropy of activation, T - temperature, k - Boltzmann constant and h - Planck’s constant.

Dividing both sides by T,

$$k_1/T = k/h\, e^{\Delta S\# / R}\, e\text{-}^{\Delta H\# / RT}$$

Taking logarithm

$$\log (k_1/T) = [\log (k/h) + \Delta S/2.303R] - (\Delta H / 2.303R)\ 1/T$$

A plot of $\log (k_1/T)$ Vs $1/T$ gave a straight line with slopes $(-\Delta H/ 2.303R)$ and intercept $(\log k/h + \Delta S/2.303R)$.

The enthalpy of activation and entropy of activation were calculated from the slopes and intercept respectively.

Polymerisation Tests with Acrylamide:

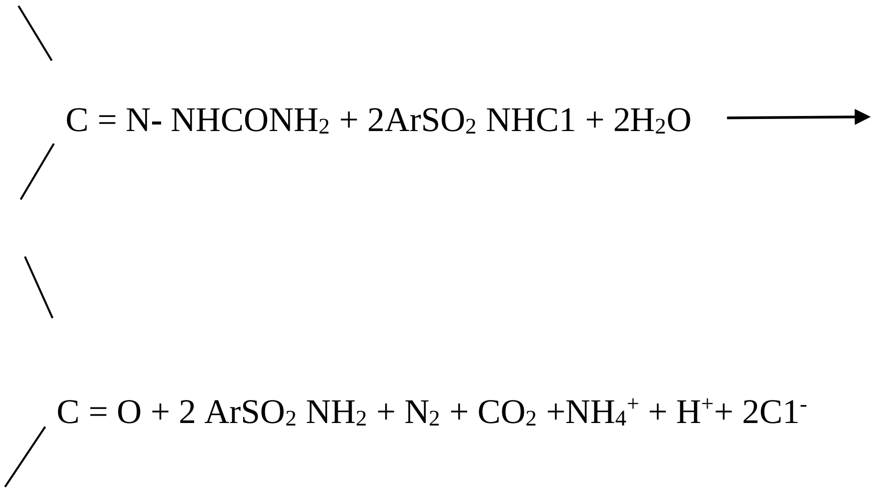
The existence of free radicals in the reaction mixtures was tested by adding a saturated solution (15 ml) of acrylamide to 5 ml of a mixture containing 0.05 mole of substrate (1), 1M perchloric acid, 0.025 mole of CAT in 25% (v/v) aqueous acetic acid.

The resulting solution was kept in a thermostat at 308K for 24 hours. No visible change was observed indicating the absence of free radical intermediates in this reaction.

Investigation Of Stoichiometry of The Reaction:

The stoichiometry of the reaction was determined by titrating the substrate with known excess of the oxidant, allowing sufficient time for completion of the reaction and then estimating the unused oxidant.

In a typical experiment propanonesemicarbazone (1) (0.03 M), CAT (0.18M) ,1 M perchloric acid in aqueous acetic 25% (v/v) was kept in a thermostat at 303 K, and the reaction was allowed to go for completion. The concentration of the unreacted oxidant was determined iodometrically. From the initial and final concentration of the oxidant, the amount reacted was determined. 1 mole of the substrate was found to consume 2 moles of the oxidant.



$$C = N\text{-}NHCONH_2 + 2ArSO_2\,NHC1 + 2H_2O \longrightarrow$$

$$C = O + 2\,ArSO_2\,NH_2 + N_2 + CO_2 + NH_4^+ + H^+ + 2C1^-$$

Product Analysis:

Oxidation of ketone semicarbazones by CAT resulted in the formation of corresponding ketone. In a typical experiment, a solution (20 ml) containing the propanonesemicarbazone **(1)** (0.1M), CAT (0.2M) and perchloric acid

(1M) in aqueous acetic acid 25% (v/v) was kept at 303K and allowed to go for completion. Liberation of CO_2 is observed as the gas evolved turned limewater milky. The reaction mixture was cooled to room temperature and then extracted with ether (4 × 30ml). The aqueous layer was separated. The ammonium ion in the aqueous layer was identified by usual Nessler's test and the presence of chloride ion using silver nitrate. The ether extracts were dried (sodium sulphate) and evaporated. The product obtained was identified as propanone using 2,4 - dinitrophenylhydrazine. Melting point of the hydrazone formed coincided with that of authentic sample.

Chapter 3

List of Tables

Table - 1

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-3}M   [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M   Temp. = 308 K

V_∞ = 13.20 ml

V_0 = 9.75 ml

$V_\infty - V_0$ = 3.45 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
600	10.25	2.95	0.4698
1020	10.65	2.55	0.4065
1560	11.10	2.10	0.3222
1980	11.40	1.80	0.2552
2580	11.70	1.50	0.1760
3060	11.90	1.30	0.1139
3780	12.15	1.05	0.0211

Slope = 8.333×10^{-3}

$k_1 = 3.183 \times 10^{-4}\ s^{-1}$

Table - 2

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2}M [$HClO_4$] = 1M

[CAT] = 1.491×10^{-3} M Temp. = 308 K

$V_\infty = 13.45$ ml

$V_0 = 6.75$ ml

$(V_\infty - V_0) = 6.70$ ml

Time (Seconds)	**V_t (m1)**	**$(V_\infty - V_t)$ (m1)**	**log $(V_\infty - V_t)$**
480	7.70	5.75	0.7596
840	8.40	5.05	0.7032
1200	8.85	4.60	0.6627
1680	9.65	3.80	0.5797
2040	10.00	3.45	0.5378
2400	10.35	3.10	0.4914
2760	10.75	2.70	0.4313

Slope = 8.571×10^{-3}

$k_1 = 3.290 \times 10^{-4}\ s^{-1}$

Table - 3

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.740×10^{-3} M Temp. = 308 K

$V_\infty = 13.60$ml

$V_0 = 5.10$ ml

$V_\infty - V_0 = 8.50$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
300	5.85	7.75	0.8893
600	6.50	7.10	0.8512
900	7.20	6.40	0.8061
1380	7.95	5.65	0.7520
1800	8.60	5.00	0.6989
2100	9.15	4.45	0.6483
2520	9.60	4.00	0.6020

Slope = 8.000×10^{-3}

$k_1 = 3.070 \times 10^{-4}\ s^{-1}$

Table - 4

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 3.908×10^{-2}M [HCIO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 13.05$ ml

$V_0 = 9.85$ ml

$V_\infty - V_0 = 3.20$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
900	10.60	2.45	0.3891
1260	10.85	2.20	0.3434
1620	11.05	2.00	0.3010
1980	11.25	1.80	0.2552
2340	11.45	1.60	0.2041
2940	11.70	1.35	0.1303
3660	11.95	1.10	0.0413

Slope = 7.680×10^{-3}

$k_1 = 2.947 \times 10^{-4}\ s^{-1}$

Table - 5

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 6.514×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 13.15$ ml

$V_0 = 10.00$ ml

$V_\infty - V_0 = 3.15$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
600	10.55	2.60	0.4150
1080	11.00	2.15	0.3324
1500	11.30	1.85	0.2671
1860	11.45	1.70	0.2304
2280	11.75	1.40	0.1461
2580	11.85	1.30	0.1139
2880	12.00	1.15	0.0606

Slope = 9.090×10^{-3}

$k_1 = 3.489 \times 10^{-4}\ s^{-1}$

Table - 6

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 7.817×10^{-2}M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 13.15$ ml

$V_0 = 9.20$ ml

$V_\infty - V_0 = 3.95$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
420	9.70	3.45	0.5378
900	10.25	2.90	0.4623
1320	10.60	2.55	0.4065
1800	11.05	2.10	0.3222
2220	11.30	1.85	0.2671
2700	11.65	1.50	0.1760
3180	11.85	1.30	0.1139

Slope = 9.677×10^{-3}

$k_1 = 3.714 \times 10^{-4}$ s^{-1}

Table - 7

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 9.119×10^{-2}M   [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M   Temp. = 308 K

V_∞ = 16.45 ml

V_0 = 10.10 ml

$V_\infty - V_0$ = 6.35 ml

Time (Seconds)	V_t (m1)	$(V_\infty - V_t)$ (m1)	log $(V_\infty - V_t)$
300	10.80	5.65	0.7520
600	11.45	5.00	0.6989
900	11.90	4.55	0.6580
1200	12.50	3.95	0.5965
1500	12.85	3.60	0.5563
1800	13.30	3.15	0.4983
2100	13.65	2.80	0.4471

Slope = 1.015×10^{-2}

$k_1 = 3.897 \times 10^{-4}\ s^{-1}$

Table - 8

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211 x 10^{-2}M [$HClO_4$] = 1M

[CAT] = 1.243 x 10^{-3} M Temp. = 308 K

V_∞ = 13.30 ml

V_0 = 9.85 ml

$V_\infty - V_0$ = 3.45 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
540	10.60	2.70	0.4313
960	10.95	2.35	0.3710
1320	11.30	2.00	0.3010
1920	11.70	1.60	0.2041
2220	11.90	1.40	0.1461
2520	12.05	1.25	0.0969
3000	12.25	1.05	0.0212

Slope = 1.040x 10^{-2}

k_1 = 3.991 x 10^{-4} s^{-1}

Table - 9

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2}M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 15.65$ ml

$V_0 = 12.50$ ml

$V_\infty - V_0 = 3.415$ ml

Time (Seconds)	**V_t (m1)**	**$(V_\infty - V_t)$ (m1)**	**log $(V_\infty - V_t)$**
660	13.20	2.45	0.3892
960	13.50	2.15	0.3324
1320	13.75	1.90	0.2788
1680	14.00	1.65	0.2175
1980	14.15	1.50	0.1761
2340	14.35	1.30	0.1139
2760	14.55	1.10	0.0414

Slope = 1.000×10^{-2}

$k_1 = 3.838 \times 10^{-4}\ s^{-1}$

Table - 10

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 15.50$ ml

$V_0 = 2.25$ ml

$V_\infty - V_0 = 12.75$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
660	6.00	9.00	0.9542
1020	7.20	7.80	0.8921
1380	8.10	6.90	0.8388
1800	9.05	5.95	0.7745
2220	9.90	5.10	0.7076
2700	10.75	4.25	0.6284
3180	11.45	3.55	0.5502

Slope = 9.625×10^{-3}

$k_1 = 3.694 \times 10^{-4}\ s^{-1}$

Table - 11

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[$NaClO_4$] = 0.1M

[Substrate] = 5.211×10^{-2} M

[$HClO_4$] = 1.1M

[CAT] = 1.243×10^{-3} M

Temp. = 308 K

V_∞ = 14.95 ml

V_0 = 10.80 ml

$(V_\infty - V_0)$ = 4.15 ml

Time (Seconds)	**V_t (m1)**	**$(V_\infty - V_t)$ (m1)**	**log $(V_\infty - V_t)$**
780	11.80	3.15	0.4983
1140	12.15	2.80	0.4472
1500	12.50	2.45	0.3892
1920	12.75	2.20	0.3423
2400	13.15	1.80	0.2553
2880	13.45	1.50	0.1761
3420	13.75	1.20	0.0792

Slope = 9.250×10^{-3}

k_1 = 3.550×10^{-4} s^{-1}

Table - 12

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v) [$NaClO_4$] = 0.05M

[Substrate] = 5.211 x 10^{-2} M [$HClO_4$] = 1.15M

[CAT] = 1.243 x 10^{-3} M Temp. = 308 K

V_∞ = 13.90 ml

V_0 = 5.20 ml

$V_\infty - V_0$ = 8.70 ml

Time (Seconds)	V_t (m1)	($V_\infty - V_t$) (m1)	log ($V_\infty - V_t$)
840	7.30	6.60	0.8200
1200	8.05	5.85	0.7671
1560	8.80	5.10	0.7053
1980	9.45	4.45	0.6484
2400	10.15	3.75	0.5740
2820	10.60	3.30	0.5185
3300	11.10	2.80	0.4472

Slope = 8.936 x 10^{-3}

k_1= 3.430 x 10^{-4} s^{-1}

Table - 13

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v) $[NaClO_4] = 0.1M$

[Substrate] = 5.211×10^{-2} M $[HClO_4] = 1M$

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 14.85$ ml

$V_0 = 10.55$ ml

$V_\infty - V_0 = 4.30$ ml

Time (Seconds)	**V_t (m1)**	**$(V_\infty - V_t)$ (m1)**	**log $(V_\infty - V_t)$**
720	11.60	3.25	0.5119
1080	12.05	2.80	0.4470
1500	12.45	2.40	0.3810
1980	12.85	2.00	0.3010
2400	13.15	1.70	0.2304
2820	13.45	1.40	0.1461
3300	13.65	1.20	0.0792

Slope = 1.029×10^{-3}

$k_1 = 3.950 \times 10^{-4}\ s^{-1}$

Table - 14

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)   [$NaClO_4$] = 0.3M

[Substrate] = 5.211×10^{-2} M   [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M   Temp. = 308 K

V_∞ = 13.80 ml

V_0 = 5.70 ml

$V_\infty - V_0$ = 8.10 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
720	7.60	6.20	0.9542
1140	8.55	5.25	0.8921
1560	9.20	4.60	0.8388
1980	9.90	3.90	0.7745
2460	10.60	3.20	0.7076
2760	10.90	2.90	0.4644
3180	11.35	2.45	0.3892

Slope = 9.818×10^{-3}

$k_1 = 3.768 \times 10^{-4}\ s^{-1}$

Table - 15

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v) [$NaClO_4$] = 0.3M

[Substrate] = 5.211 x 10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243 x 10^{-3} M Temp. = 308 K

V_∞ = 14.85 ml

V_0 = 5.35 ml

$V_\infty - V_0$ = 12.75 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
720	7.55	7.30	0.8633
1200	8.65	6.20	0.7924
1380	9.45	5.40	0.7324
1800	10.15	4.70	0.6721
2220	10.70	4.15	0.6180
2700	11.20	3.65	0.5623
3180	11.65	3.20	0.5051

Slope = 9.924 x 10^{-3}

k_1 = 3.809 x 10^{-4} s^{-1}

Table - 16

Substrate = Propanone semicarbazone **(1)**

Solvent = 30% AcOH - 70% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp.= 308 K

$V_\infty = 13.40$ ml

$V_0 = 9.75$ ml

$V_\infty - V_0 = 3.65$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
600	10.40	3.00	0.4771
1080	10.95	2.45	0.3891
1500	11.30	2.10	0.3222
1860	11.50	1.90	0.2787
2280	11.70	1.70	0.2304
2580	11.95	1.45	0.1613
3180	12.15	1.25	0.0969

Slope = 9.032×10^{-3}

$k_1 = 3.467 \times 10^{-4}\ s^{-1}$

Table - 17

Substrate = Propanone semicarbazone **(1)**

Solvent = 35% AcOH - 65% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 13.25$ ml

$V_0 = 8.95$ ml

$V_\infty - V_0 = 4.30$ ml

Time (Seconds)	V_t (m1)	$(V_\infty - V_t)$ (m1)	log $(V_\infty - V_t)$
480	9.65	3.60	0.5563
1080	10.40	2.85	0.4548
1560	10.85	2.40	0.3802
1920	11.20	2.05	0.3117
2280	11.45	1.80	0.2552
2760	11.75	1.50	0.1761
3360	12.05	1.20	0.0791

Slope = 1.008×10^{-3}

$k_1 = 3.871 \times 10^{-4}\ s^{-1}$

Table - 18

Substrate = Propanone semicarbazone (1)

Solvent = 40% AcOH - 60% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [HCIO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

V_∞ = 13.25 ml

V_0 = 8.75 ml

$V_\infty - V_0$ = 4.50 ml

Time (Seconds)	**V_t (m1)**	**$(V_\infty - V_t)$ (m1)**	**log $(V_\infty - V_t)$**
480	9.60	3.65	0.5622
1080	10.40	2.85	0.4548
1560	10.85	2.40	0.3802
1920	11.25	2.00	0.3010
2280	11.45	1.80	0.2552
2760	11.85	1.40	0.1461
3180	12.05	1.20	0.0791

Slope = 1.093×10^{-3}

$k_1 = 4.195 \times 10^{-4}\ s^{-1}$

Table - 19

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v) [p-tol.sul.] = 2.920 x10^{-3}M

[Substrate] = 5.211 x 10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243 x 10^{-3} M Temp. = 308 K

V_∞= 16.65 ml

V_0 = 7.25 ml

$V_\infty - V_0$ = 9.40 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
300	8.05	8.60	0.9344
600	8.90	7.75	0.8893
900	9.65	7.00	0.8450
1260	10.50	6.15	0.7888
1620	11.00	5.65	0.7520
2100	11.90	4.75	0.6767
2520	12.40	4.25	0.6283

Slope = 8.470 x 10^{-3}

k_1 = 3.251 x 10^{-4} s^{-1}

Table - 20

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v) [p-tol.sul.] = 4.380×10^{-3}M

[Substrate] = 5.211×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

V_∞ = 15.50 ml

V_0 = 2.25 ml

$V_\infty - V_0$ = 12.75 ml

Time (Seconds)	V_t (m1)	($V_\infty - V_t$) (m1)	log ($V_\infty - V_t$)
300	11.80	3.55	0.5502
600	12.15	3.20	0.5051
900	12.55	2.80	0.4471
1320	12.90	2.45	0.3891
1760	13.20	2.15	0.3324
2040	13.40	1.95	0.2900
2400	13.60	1.75	0.2430

Slope = 8.222×10^{-3}

$k_1 = 3.157 \times 10^{-4} s^{-1}$

Table - 21

Substrate = Propanone semicarbazone (1)

Solvent = 25% AcOH - 75% H_2O (v/v)

[p-tol.sul.] = 5.840×10^{-3}M

[Substrate] = 5.211×10^{-2} M

[$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M

Temp. = 308 K

V_∞ = 14.85 ml

V_0 = 7.70 ml

$V_\infty - V_0$ = 7.15 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
300	8.35	6.50	0.8129
600	8.85	6.00	0.7781
900	9.45	5.40	0.7323
1200	10.05	4.80	0.6812
1620	10.55	4.30	0.6334
2100	11.25	3.60	0.5563
2460	11.65	3.20	0.5051

Slope = 8.625×10^{-3}

$k_1 = 3.311 \times 10^{-4}\ s^{-1}$

Table - 22

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [$HCIO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 303 K

$V_\infty = 15.50$ ml

$V_0 = 11.25$ ml

$V_\infty - V_0 = 4.25$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
900	12.05	3.45	0.5378
1260	12.35	3.15	0.4983
1800	12.80	2.70	0.4313
2400	13.20	2.30	0.3617
2880	13.50	2.00	0.3010
3540	13.80	1.70	0.2304
4200	14.10	1.40	0.1461

Slope = 6.756×10^{-3}

$k_1 = 2.593 \times 10^{-4}\ s^{-1}$

Table - 23

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211 x 10^{-2} M [HCIO$_4$] = 1M

[CAT] = 1.243 x 10^{-3} M Temp. = 313 K

V_∞ = 15.70 ml

V_0 = 9.30 ml

$V_\infty - V_0$ = 6.40 ml

Time (Seconds)	V_t (m1)	$(V_\infty - V_t)$ (m1)	log $(V_\infty - V_t)$
420	10.60	5.50	0.7403
720	10.55	5.15	0.7118
1140	11.50	4.20	0.6232
1500	11.95	3.75	0.5740
1860	12.15	3.30	0.5185
2340	13.00	2.70	0.4313
2700	13.35	2.35	0.3710

Slope = 9.545x 10^{-3}

k_1 = 3.663 x 10^{-4} s^{-1}

Table - 24

Substrate = Propanone semicarbazone **(1)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 5.211×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 318 K

V_∞ = 15.55 ml

V_0 = 9.70 ml

$V_\infty - V_0$ = 5.85 ml

Time (Seconds)	V_t (m1)	($V_\infty - V_t$) (m1)	log ($V_\infty - V_t$)
300	10.40	5.15	0.7118
900	11.55	4.00	0.6020
1320	12.15	3.40	0.5314
1620	12.55	3.00	0.4771
1920	12.95	2.60	0.4149
2400	13.35	2.20	0.3424
2700	13.65	1.90	0.2788

Slope = 1.076×10^{-2}

k_1 = 4.134×10^{-4} s^{-1}

Table - 25

Substrate = Butanone semicarbazone **(2)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.645×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 303 K

V_∞ = 15.75 ml

V_0 = 6.95 ml

$V_\infty - V_0$ = 8.80 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
780	8.75	7.00	0.8451
1140	9.55	6.20	0.7924
1500	10.25	5.50	0.7404
1920	11.00	4.75	0.6767
2400	11.60	4.15	0.6180
2880	12.25	3.50	0.5502
3480	12.85	2.90	0.4624

Slope = 7.520×10^{-3}

$k_1 = 2.886 \times 10^{-4}\ s^{-1}$

Table - 26

Substrate = Butanone semicarbazone **(2)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.645×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 16.75$ ml

$V_0 = 12.05$ ml

$V_\infty - V_0 = 4.70$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
480	12.75	4.00	0.6021
900	13.30	3.45	0.5378
1260	13.70	3.05	0.4843
1620	14.00	2.75	0.4393
2100	14.40	2.35	0.3711
2460	14.70	2.05	0.3118
2940	15.00	1.75	0.2430

Slope = 8.818×10^{-3}

$k_1 = 3.385 \times 10^{-4}\ s^{-1}$

Table - 27

Substrate = Butanone semicarbazone **(2)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.645×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

V_∞ = 15.70 ml

V_0 = 8.65 ml

$V_\infty - V_0$ = 7.05 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
420	9.80	5.90	0.7709
840	10.65	5.05	0.7033
1200	11.50	4.20	0.6232
1560	12.05	3.65	0.5623
1980	12.60	3.10	0.4914
2400	13.10	2.60	0.4150
3000	13.70	2.00	0.3010

Slope = 1.075×10^{-2}

$k_1 = 4.126 \times 10^{-4}\ s^{-1}$

Table - 28

Substrate = Butanone semicarbazone **(2)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.645×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 318 K

$V_\infty = 16.50$ ml

$V_0 = 6.95$ ml

$V_\infty - V_0 = 9.55$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
300	8.20	8.30	0.9791
720	9.60	6.90	0.8388
1140	10.85	5.65	0.7520
1620	11.95	4.55	0.6580
2100	12.85	3.65	0.5623
2580	13.65	2.85	0.4548
3000	14.15	2.35	0.3711

Slope = 1.200×10^{-2}

$k_1 = 4.606 \times 10^{-4}\ s^{-1}$

Table - 29

Substrate = 3-Pentanone semicarbazone **(3)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.219×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 303 K

$V_\infty = 15.35$ ml

$V_0 = 9.25$ ml

$V_\infty - V_0 = 6.10$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
600	10.20	5.15	0.7118
960	10.85	4.50	0.6532
1320	11.25	4.00	0.6021
1740	11.85	3.50	0.5441
2160	12.30	3.05	0.4843
2700	12.75	2.60	0.4150
3420	13.30	2.05	0.3118

Slope = 8.353×10^{-3}

$k_1 = 3.206 \times 10^{-4}\ s^{-1}$

Table - 30

Substrate = 3-Pentanone semicarbazone **(3)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.219×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 308 K

$V_\infty = 14.45$ ml

$V_0 = 6.60$ml

$V_\infty - V_0 = 7.85$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
420	7.55	6.90	0.8388
900	8.75	5.70	0.7559
1260	9.70	4.75	0.6767
1620	10.30	4.15	0.6180
1980	10.80	3.65	0.5623
2400	11.30	3.15	0.4983
2880	11.80	2.65	0.4232

Slope = 9.428×10^{-3}

$k_1 = 3.618 \times 10^{-4}\ s^{-1}$

Table - 31

Substrate = 3-Pentanone semicarbazone **(3)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.219×10^{-2} M [HClO$_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp. = 313 K

$V_\infty = 16.25$ ml

$V_0 = 9.40$ ml

$V_\infty - V_0 = 6.85$ ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
360	10.25	6.00	0.7782
780	11.50	4.75	0.6767
1200	12.30	3.95	0.5966
1560	12.90	3.35	0.5250
1980	13.50	2.75	0.4393
2400	13.90	2.35	0.3711
3000	14.45	1.80	0.2553

Slope = 1.171×10^{-2}

$k_1 = 4.493 \times 10^{-4}\ s^{-1}$

Table - 32

Substrate = 3-Pentanone semicarbazone **(3)**

Solvent = 25% AcOH - 75% H_2O (v/v)

[Substrate] = 4.219×10^{-2} M [$HClO_4$] = 1M

[CAT] = 1.243×10^{-3} M Temp.= 318 K

V_∞ = 16.15 ml

V_0 = 7.10 ml

$V_\infty - V_0$ = 9.05 ml

Time (Seconds)	**V_t (m1)**	**($V_\infty - V_t$) (m1)**	**log ($V_\infty - V_t$)**
300	8.20	7.95	0.9004
660	9.45	6.70	0.8261
1080	10.85	5.30	0.7243
1500	11.90	4.25	0.6284
1960	12.60	3.55	0.5502
2340	13.30	2.85	0.4548
2940	14.15	2.00	0.3010

Slope = 1.320×10^{-3}

$k_1 = 5.066 \times 10^{-4}\ s^{-1}$

Chapter 4

Results and Discussion

Kinetics of oxidation of aliphatic ketone semicarbazones (1) - (3) by chloramine - T (CAT) has been investigated at constant ionic strength in 25% - 40% (v/v) aqueous acetic acid in the presence of perchloric acid (1M) in the temperature range at 303K - 318K and the results are recorded in Table 1 - 43.

Dependence of Rate on [CAT]:

The kinetics of oxidation of semicarbazones have been investigated maintaining pseudo first order conditions, keeping the concentrations of semicarbazones in multifold excess (more than 10 folds) over that of [CAT].

When log $[CAT]_T$ is plotted against time, very good straight-line plots are obtained indicating that the reaction follows first order kinetics with respect to [CAT].

The data of kinetic runs of the oxidation of propanonesemicarbazone **(1)** are given in Table - 1 and the corresponding first order plots, as a representative example, is shown in Figure - 1.

The progress of the reaction was monitored for at least two half-lives by the iodometric estimation of unreacted oxidant at regular intervals.

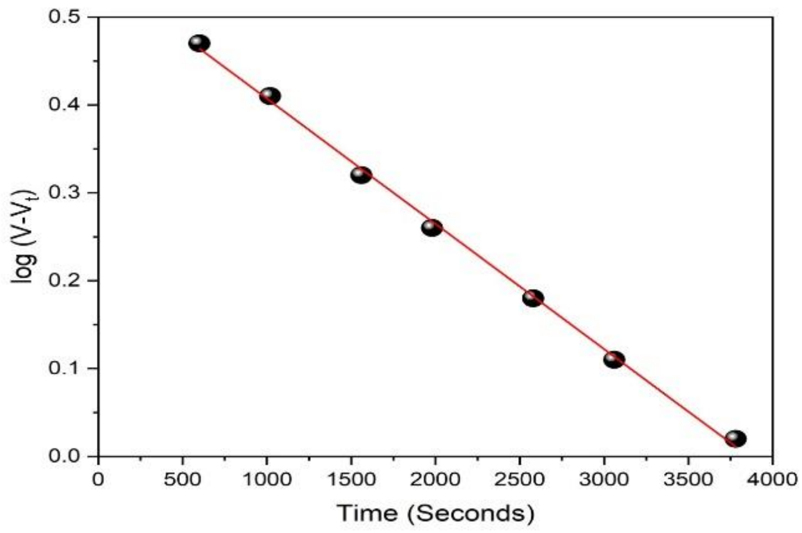


Figure 1: log (V_∞ – V_t) Vs Time

Effect of varying [CAT] on the rate of oxidation has also been studied at constant [substrate] and [H_3O+] and the results are given in Table - 33.

The pseudo first order rate constants computed from the plots of log $[CAT]_T$ Vs Time are unaffected by the changes in [CAT], confirming the first order dependence of rate on [CAT].

Dependence of Rate on [Substrate]:

The results recorded in Table - 34 indicate the dependence of rate when [substrate] is varied at constant [CAT] and [H_3O+]. The reaction rate increased progressively with increase in [substrate]. The plot of log k_1 against log [substrate] is a straight line with fractional slope (~ 0.36) (Figure-2). Thus, the reaction has fractional order dependence on [substrate].

Dependence of Rate on [H_3O+]:

The oxidation of propanonesemicarbazone (1) has been studied in the range of 0.95M - 1.15M perchloric acid at constant ionic strength in 25% (v/v) aqueous acetic acid at 308K and the results are recorded in Table - 35. Ionic strength of the medium was maintained using sodium perchlorate. The data indicate that with increase in [H_3O^+], there is a liner decrease in rate constant values.

Dependence of Rate on The Concentration of Chloramine - T (CAT):

Subtrate = Propanonesemicarbazone **(1)**

Solvent = 25% AcOH - 75% [H_3O^+] (v/v)

[Substrate] = 5.211×10^{-2} M

[$HC1O_4$] = 1M

Temp = 308 K

Table - 33

[Oxidant] / 10^{-4} M	**$k_1/10^{-5}$ s^{-1}**
12.13	31.83
14.91	32.90
17.39	30.70

Dependence of Rate on Substrate Concentration:

Subtrate = Propanonesemicarbazone **(1)**

Solvent = 25% AcOH - 75% [H_3O^+] (v/v)

[Substrate] = 1.243 x 10^{-3}M

[$HC1O_4$] = 1M

Temp = 308 K

Table – 34

[S] / 10-5 M	**$k_1/10^{-5}$ s^{-1}**
39.08	29.47
52.11	31.83
65.14	34.89
78.17	37.14
91.19	38.97

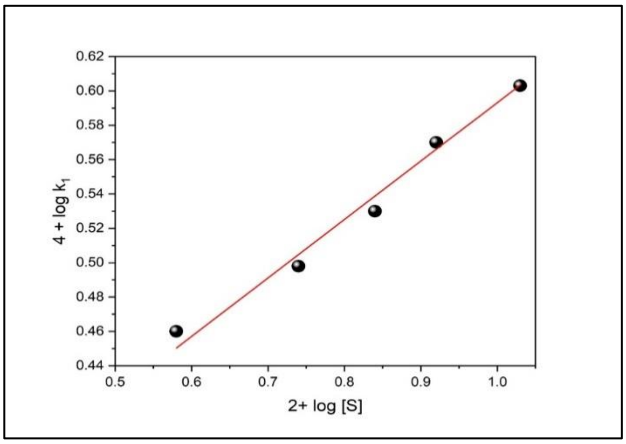


Figure 2: logk_1 Vs log [S]

Effect of the Concentration of Perchloric Acid on Reaction Rate:

Subtrate = Propanonesemicarbazone **(1)**

Solvent = 25% AcOH - 75% [H_3O^+] (v/v)

[Substrate] = 5.211 x 10^{-2}M

[CAT] = 1.243 X 10^{-3} M

Temp = 308 K

Table - 35

[HC1O$_4$] M	[NaClO$_4$] M	$k_1/10^{-5}$ s^{-1}
0.95	0.25	39.91
1.00	0.20	38.38

$[HC1O_4]$ M	$[NaCIO_4]$ M	$k_1/10^{-5}$ s^{-1}
1.05	0.15	36.94
1.10	0.10	35.50
1.15	0.05	34.30

Also, a plot of log [1/ k_1] Vs log $[H_3O^+]$ gave a straight line. The order with respect to $[H_3O+]$ is found to be fractional (= 0.78) (Figure - 3). Thus, the reaction has inverse fractional order dependence on $[H_3O^+]$**.**

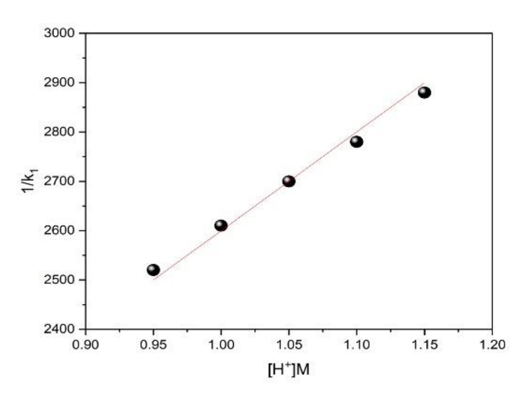


Figure 3: log 1/k_1 Vs log $[H^+]$

Effect of Added Neutral Salts:

The oxidation of propanonesemicarbazone **(1)** by CAT in the presence of added neutral salt, sodium perchlorate, has been investigated in 25% (v/v) aqueous acetic acid and the results are given in Table - 36. The data reveal that the reaction is not that much susceptible to ionic strength variations of the medium in the range of 0.1 M - 0.4 M.

Dependence of Rate on Solvent Polarity of The Medium:

The rate dependence on solvent polarity of the medium is studied by varying the acetic acid content of the reaction mixture from 25% - 40% (v/v) in the oxidation of propanonesemicarbazone (1) and the results are recorded in Table- 37. The rate of the oxidation increases with increase in concentration of acetic acid. Thus, a decrease in solvent polarity enhances the reaction rate. A plot of log k_1 Vs (D-1/2D+1) where D is the dielectric constant of the medium gave a straight line ^{64} (Figure - 4). This indicates that in the rate determining step of the

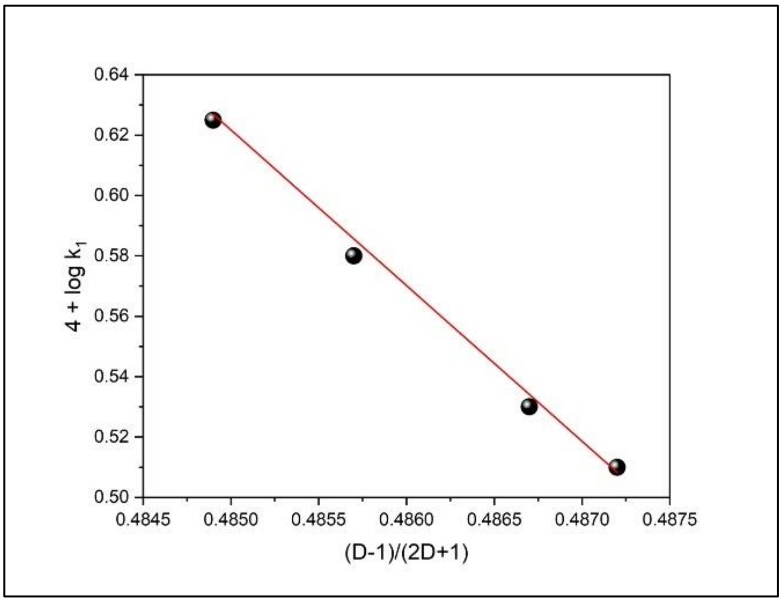


Figure 4: logk$_1$ Vs (D-1) (2D+1)

Effect Of Ionic Strength on The Reaction Rate

Substrate = Propanone semicarbazone **(1)**

Solvent = 25%AcOH - 75% H_2O(v/v)

[Substrate] = 5.211×10^{-2} M

[CAT] = 1.243×10^{-3} M

[$HClO_4$] = 1 M

Temp = 308 K

Table - 36

[$NaClO_4$] M	**$k_1/10^{-5}\ s^{-1}$**
0.1	39.50
0.2	38.38
0.3	37.68
0.4	38.09

Effect of Varying Solvent Polarity on The Reaction Rate

Substrate = Propanone semicarbazone **(1)**

Solvent = 25%AcOH - 75% H_2O

[Substrate] = 5.211×10^{-2} M

[CAT] = 1.243×10^{-3} M

[$HClO_4$] = 1M

Temp. = 308 K

Table - 37

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

reaction there is an interaction between two dipoles or an ion and a dipole. The D values of acetic acid-water mixture are not readily available in the literature and attempts to determine these values are not fruitful. One has therefore been forced to approximate the values on the basis of data for pure acetic acid and water[65], assuming a linear relationship in the range of solvent composition used in the present study. A similar approximation has been made by Wiberg and Evans[66] with regard to this binary solvent system.

Test for the presence of free radicals: Free radicals as intermediates during the course of the reaction are ruled out since the reaction mixture failed to induce the polymerisation of added acrylamide. A detailed study has been already given in the experimental section.

Effect of Added P-Toluene Sulphonamide on Reaction Rate:

Effect of p-toluenesulphonamide, one of the reaction products on the reaction rate is studied in the case of propanone semicarbazone (1) and the results are given in Table - 38.

The data reveal that the reaction rate is not susceptible to change in [p-toluenesulphonamide]. This indicates that p-toluenesulphonamide is not formed in a pre-equilibrium step.

Effect of Added P-Toluenesulphonamide on The Reaction Rate:

Substrate = Propanone semicarbazone **(1)**

[Substrate] = 5.211×10^{-2} M

[CAT] = 1.243×10^{-3} M

[HCIO4] = 1M

Temp. = 308 K

Table - 38

[p- toluenesulphonamide]. /10-4 M	k1/10-5 s-1
0	31.83
29.20	32.51
43.80	31.57
58.40	33.11

Effect of Temperature and Evaluation of Activation Parameters:

The reaction was conducted at several temperatures in the range 303K-318 K (Table-39). A plot of log (k_1/T) Vs1/T is drawn. The plot obtained for propanone semicarbazone **(1)** is represented in Figure - 5.

Form the slope and the intercept the enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) are calculated (Table -40). The observed negative entropy of activation indicates that transition state of the rate limiting step is more ordered than the initial step.

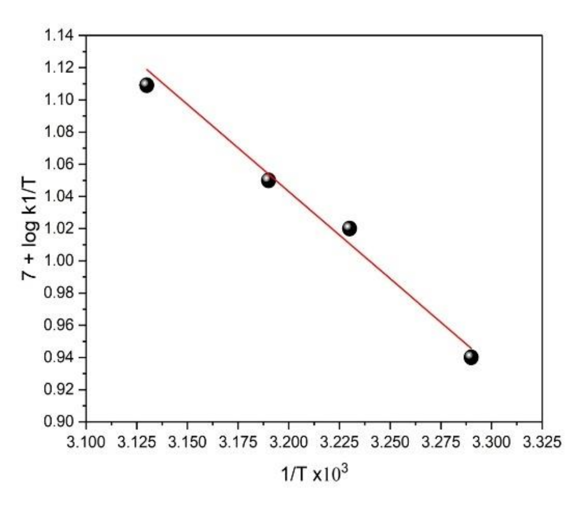


Figure 5: log k_1/T Vs 1/T

Effect of Structural Variation:

Kinetics of oxidation of propanone semicarbazone **(1)**, butanone semicarbazone **(2)** and 3- pentanone semicarbazone **(3)** by CAT have been investigated under identical conditions and the rate constants are given in the Table - 41.

Nature of Oxidant Species:

Chloramine - T (N – chloro – N - sodio - p-toluenesulphonamide), $ArSO_2NCINa$, where ($Ar = C_6H_4CH_3$) is fairly a strong electrolyte [67-69] in aqueous solutions.

Effect of Temperature on the Reaction Rate:

Solvent = 25%AcOH - 75% H_2O

[CAT] = 1.243×10^{-3} M

[$HClO_4$] = 1M

Table – 39

Temperature K	**$k_1/10^{-5}\ s^{-1}$**
Propanone semicarbazone **(1)**	
303	25.93
308	31.83
313	36.63
318	41.34
Butanone semicarbazone **(2)**	
303	28.86
308	33.85
313	41.26
318	46.06

Temperature K	**$k_1/10^{-5}\ s^{-1}$**
3- Pentanone semicarbazone **(3)**	32.06
303	36.18
308	44.93
313	50.66
318	

Evaluation of Activation Parameters:

[CAT] = 1.243×10^{-3} M

Solvent = 25%AcOH - 75% H_2O

$[HClO_4]$ = 1M

Table - 40

Compound	**$\Delta H^{\#}$ K J mol-1**	**$\Delta S^{\#}$ J mol-1K -1**
(1)	23.45	-105.47
(2)	23.93	-102.79
(3)	22.97	-100.68

Effect of Structure on Rate:

[CAT] = 1.243×10^{-3} M

Solvent = 25%AcOH - 75% H_2O

[HCIO4] = 1M

Temp. = 308 K

Table - 41

Compound	[Substrate]/ 10^{-3} M	$k_1/10^{-5}$ s^{-1}
(1)	52.11	31.83
(2)	46.45	33.85
(3)	42.19	36.18

It furnishes different types of reactive species in aqueous and partial aqueous solutions depending upon pH of the medium,due to presence of following equilibria,

$$ArSO_2NCl\,Na \rightleftharpoons ArSO_2NCl^- + Na^+ \quad \text{------------ (1)}$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl \qquad \text{------------ (2)}$$

$$(K_a = 2.82 \times 10^{-5} \text{ at } 25^oC)$$

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NCl_2 + ArSO_2NH_2 \qquad \text{------------ (3)}$$

$$(K_d = 5.80 \times 10^{-2} \text{ at } 25^oC)$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl \qquad \text{------------ (4)}$$

$$(K_h = 4.88 \times 10^{-4} \text{ at } 25^oC)$$

$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl \qquad \text{------------ (5)}$$

$$(Kh^1 = 8 \times 10^{-7} \text{ at } 25^oC)$$

$$ArSO_2NHCl + H^+ \rightleftharpoons ArSO_2NH_2Cl^+ \qquad \text{------------ (6)}$$

$$ArSO_2NH_2Cl^+ + H_2O \rightleftharpoons ArSO_2NH_2 + H_2OCl^+ \qquad \text{------------ (7)}$$

Thus the possible oxidising species in acid solution of CAT are $ArSO_2NCl^-$; $ArSO_2NHCl$; HOCl; $ArSO_2NH_2Cl^+$ and H_2OCl^+ Under the present experimental conditions at $[HCIO_4]$ = 1 M the possible oxidising species may be $ArSO_2NH_2Cl^+$ and H_2OCl^+. A similar consideration regarding CAT has been given by B.Thimme Gowda and J.I.Bhat[70] in 0.1 M $HClO_4$ solutions. If H_2OCl^+ is the active specie, retardation of rate by the added p-toluenesulphonamide could be expected because of the equilibria (7). But no such effect is observed in this reaction (Table – 32). This rules out H_2OCl^+ as the possible oxidising specie.Hence in the present investigation $ArSO_2NH_2Cl^+$ is assumed to be the active species.

Mechanism And Rate Law: The observed results in the oxidation of semicarbazones of various aliphatic ketones (1) – (3) may be explained by the reaction pathway shown in Scheme – 5.

$$ArSO_2NH_2CI^+ + S \quad \rightarrow \quad \text{Complex} + H^+$$

$$(CATH^+) \rightleftharpoons \qquad \text{(Y)} \qquad \text{--------(8)}$$

$$\text{Complex}$$

$$\text{(Y)} \qquad \overset{ks}{\rightarrow} \quad \text{Y'} \qquad \text{--------(9)}$$

$$\text{Y'}+H_2O \qquad \xrightarrow{Fast} \quad \text{X}+ArSO_2NH_2 \qquad \text{--------(10)}$$

$$\text{X}+ArSO_2NH_2CI^+ \xrightarrow{Fast} \quad \text{Products} \qquad \text{--------(11)}$$

Where S is the ketone semicarbazone

Scheme – 5

Based on Scheme – 5, the following rate law can be deduced.

$$\text{Rate} \quad = \quad K_+ (Y) \qquad \text{---------(12)}$$

$$(CATH^+)\,T = (\text{Y}) + (CATH^+)e$$

$$K_1 \quad = \quad \frac{(Y)H^+}{(CATH^+)e(S)} \qquad \text{--------(13)}$$

$$(CATH^+)\text{e} \quad = \frac{(Y)H^+}{K_+ (S)} \qquad \text{--------(14)}$$

Substituting (14) in (13),

$$(CATH^{+})\,T = (\mathrm{Y}) + \frac{(Y)H^{+}}{K_1\,(S)}$$

$$= \frac{K_1\,(Y)(S) + (Y)H^{+}}{K_1\,(S)}$$

$$(CATH^{+})\,T = \frac{(Y)(K_1\,(S) + H^{+}}{K_1\,(S)} \qquad \text{--------(15)}$$

Substituting (15) in (12),

$$\mathrm{Rate} = \frac{K_S\,K_1(\mathrm{CATH}^{+})_{\mathrm{T}}[\mathrm{S}]}{[\mathrm{H}^{+}] + K_1\,(S)} \qquad \text{------------------- (16)}$$

(OR)

$$k_{obs} = \frac{K_S\,K_1[\mathrm{S}]}{[\mathrm{H}^{+}] + K_1\,(S)} \qquad \text{------------------- (17)}$$

(OR)

$$\frac{1}{\mathrm{K_{obs}}} = \frac{[\mathrm{H}^{+}]}{K_S\,K_1}\;\frac{1}{(S)} + \frac{1}{\mathrm{K_s}} \qquad \text{------------------- (18)}$$

(OR)

$$\frac{1}{\mathrm{K_{obs}}} = \frac{[\mathrm{H}^{+}]}{K_S\,K_1\,(S)} + \frac{1}{\mathrm{K_s}} \qquad \text{------------------- (19)}$$

Rate law (18) predicts that a plot of 1/k_{obs} Vs 1/[S] at constant [H^+] should be linear,while rate law (19) proposes a straight line plot when 1/k_{obs} is plotted against [H^+].This has been observed (Figures 6 and 7) .

Further a 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.

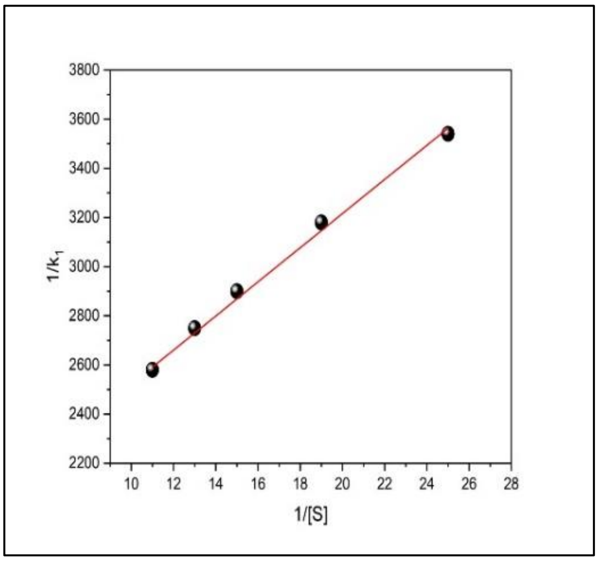


Figure 6: $1/k_1$ Vs 1/[S]

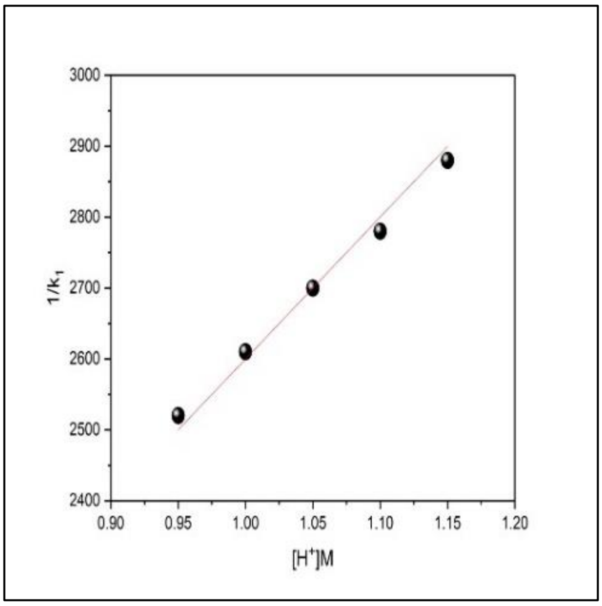
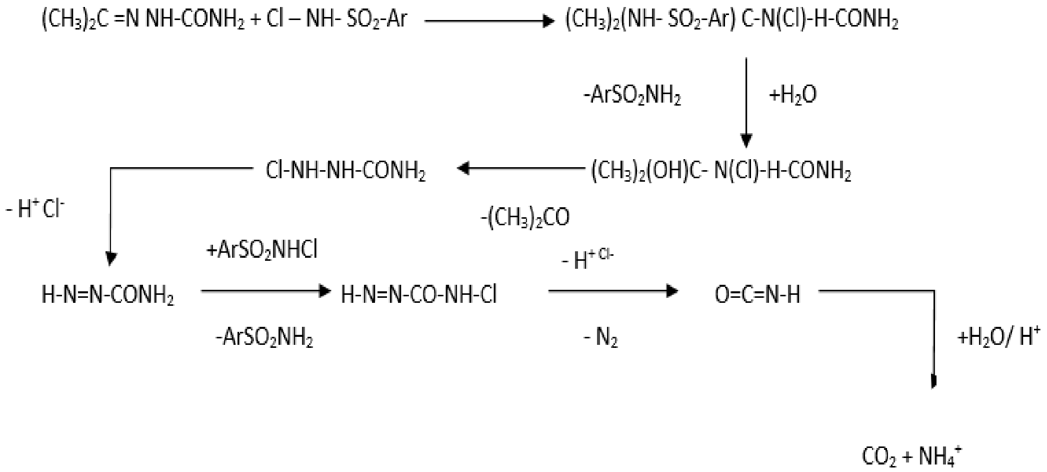


Figure 7: $1/k_1$ Vs $[H^+]$

From the plots of $1/k_{obs}$ Vs 1/[S] and $1/k_{obs}$ Vs $1/[[H^+]$ the values of constants K_1 and ks are computed. These values are used to recalculated the rate constants from the rate law.

The recalculated values and the experimental rate constants as the [substrate] are varied is shown in Table- 42 and a [H_3O^+] is varied is shown in Table-43. The data in Tables -42 and 43 reveal that the experimental and recalculated values are reasonably in good agreement, thus confirming the mechanism proposed. The observed negative entropy of activation (Table – 40) is also in consonance with the proposed mechanism which envisages coming together, in the rate limiting step of two independent species to form a single transition state species and thus resulting in the substantial loss in translational and rotational entropies.

The steps involved in the formation of reaction products is shown in scheme – 6.



Scheme – 6

Comparison of recalculated values and experimental rate constants for oxidation of propanone semicarbazone (1) in aquo – acetic acid [3:1 (v/v)] mediumin presence of perchloric acid at 308 K.

Table- 42

Conc.of Substrate/ 10^{-3} M	k_1 (Experimental)/ 10^{-5} s-1	k_1(Recalculated)/ 10^{-5} s-1
39.08	29.48	29.37
52.11	31.83	32.58
65.14	34.89	34.87
78.17	37.15	35.59
91.19	38.97	37.93

Comparison of recalculated values and experimental rate constants for oxidation of propanone semicarbazone in aquo – acetic acid [3:1 (v/v)] mediumin presence of perchloric acid at 308 K

Table - 43

Conc.of $HClO_4$ M	(Experimental)/10^{-5} s-1	k1(Recalculated)/10^{-5} s-1
0.95	39.91	38.21
1.00	38.38	36.87
1.05	36.98	35.61
1.10	35.50	34.44

Conc.of $HClO_4$ M	(Experimental)/10^{-5} s-1	k1(Recalculated)/10^{-5} s-1
1.15	34.30	33.34

Structure and Reactivity:

The mechanism shown in schemes 5 and 6 envisages the simultaneous attack of positive chlorine of $CATH^+$ on the imino nitrogen of the semicarbazone and the negative nitrogen of $CATH^+$ on the carbon attached to the imino nitrogen.

This should be facilitated by the electron releasing groups at the reaction site. This is evidenced in the data of oxidation of various ketone semicarbazone by CAT shown in Table- 41. The data reveal that the order of reactivity is Propanone semicarbazone **(1)** < Butanone semicarbazone **(2)** 3-pentanone semcarbazone **(3)**.

The observed trends may be understood by utilizing the electron releasing inductive effect of alkyl groups. As the size of alkyl group increase its electron donating ability also increases.

The imino group is attached to two methyl groups in (1), to one ethyl and one methyl group in (2) and to two ethyl groups in (3). Ethyl group is more electron donating than methyl group. (2) is more reative than (1) as one methyl group is replaced by ethyl. (3) is more reactive than (1) and (2) as it has two ethyl groups attached to imino carbon. Thus, the observed trends in the rates of oxidation of different semicarbazones by CAT can be rationalised.

Chapter 5

Summary

In the present investigation kinetics of oxidation of aliphatic ketone semicarbazones **(1) – (3)** by chloramine – T (CAT) in aqueous acetic acid in the presence of perchloric acid have been carried out.

Kinetics of oxidation of all the substrates have been carried out under pseudo first order conditions with [substrate] always in large excess over that of [oxidant] in the presence of 1M perchloric acid in 25% (v/v) aqueous acetic acid media at 308K.Ionic strength is maintained using sodium perchlorate.The activation parameters have been evaluated by conducting the reactions at several temperatures.

The following is the summary of the various observations made:

1. The reaction followed first order kinetics in the [oxidant] when concentration of the perchloric acid is maintained as constant.
2. The reaction has fractional order dependence on [substrate].
3. The reaction has inverse fractional order dependence on [H_3O^+].
4. With increase in dielectric constant of the medium the rate of the reaction is slightly increased.
5. The rate of the reaction is not greatly affected by increase in ionic strength of the medium.
6. The addition of p-toluenesulphonamide, one of the reaction products does not affect rate of the reaction.

7. Acryl amide when added failed to polymerize. Thus, the possibility of free radical mechanism is eliminated.
8. A more orderly transition state than the initial conditions is indicated by the negative entropy of activation of the reaction.
9. The effect of structural variation has been studied using three different ketone semicarbazones under identical conditions.
10. Stoichiometric studies reveal that in this reaction one mole of the substrate reacted with two moles of the oxidant.
11. The product analysis showed that the corresponding ketone, p-toluenesulphonamide,ammonium ion,chloride and carbondioxide as the reaction products

A plausible mechanism consistent with the observed facts has been proposed.The relative reactivities of the various substrates studied have been rationalised suitably.

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