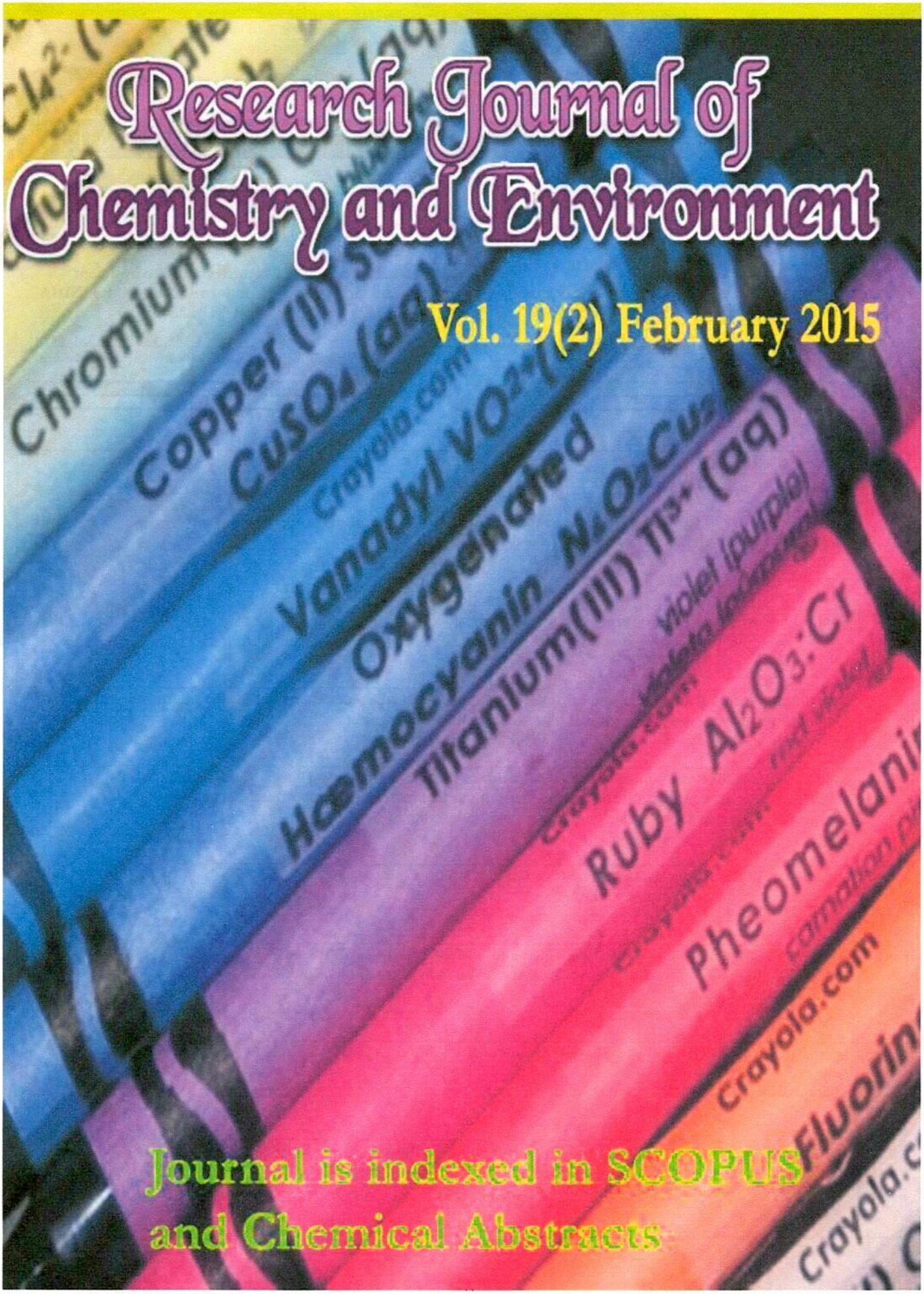
Research Journal of
Chemistry and Environment
Vol. 19(2) February 2015
Journal is indexed in SCOPUS
and Chemical Abstracts

GOD IS.

E-ISSN : 2278 – 4527

RESEARCH JOURNAL OF CHEMISTRY AND ENVIRONMENT

An International Research Journal of Chemical Sciences and Environmental Sciences
Res. J. Chem. Environ., Volume **19 (2)**, Pages 1-87, February **(2015)**

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CONTENTS

Kinetics and Mechanism of Oxidation of o, m and p Methyl Substituted Phenoxy Acetic Acid Hydrazides to their Corresponding Aryloxy Acetic Acids by Vanadium (V)

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Abstract

The kinetics and mechanism of the effect of various positions of methyl substituent in aromatic ring were studied by oxidizing o,m and p methyl substituted phenoxy acetic acid hydrazides to their corresponding aryloxy acetic acids by vanadium (v) in sulphuric acid medium under pseudo first order condition. The formation of complex between the reactants decomposes in the subsequent step to give products. The reaction proceeds by one electron transfer with intervention of free radical. Increase in hydrazide concentration decreases the specific rate. Increase in acid concentration increases the reaction rate and decreases with decrease in dielectric constant.

The effect of temperature was studied between 25 to 55 °C. The activation parameters were determined and the values support the proposed mechanism as evidenced by considerable decrease in entropy of activation ($-\Delta S^{\neq}$ = 141.68, 135.78 and 134.86 J K^{-1} mol^{-1} respective for o-Me-PAAH, m-Me-PAAH and p-Me-PAAH respectively).

Keywords: Oxidation, Kinetics, mechanism, pseudo-first order, hydrazides, vanadium (V), o-Me-PAAH, m-Me-PAAH, p-Me-PAAH.

Introduction

Oxidation is an important transformation in organic chemistry. Hydrazides are derivatives of carboxylic acids with hydrazines[9]. They have been extensively used in various fields of chemistry[3,6,10,12,21-23] for the preparation of variety biologically important molecules, therefore it is necessary to study and understand the mechanism of their oxidation by using Chemical kinetics which deals with the rate at which the chemical reactions take place and deals with the influence of various factors such as effect of position of same substituent's in aromatic ring, concentration of reactant, temperature, pressure catalysts etc. on the rates of the reaction.

Material and Methods

The preparation of the o-Me-PAAH, m-Me-PAAH and p-Me-PAAH was done by reported procedure[20] and stored in amber colored bottles kept in dark place. Ammonium metavanadate, sulphuric acid and salt used were of AR grade. The stock solution of ammonium metavanadate was prepared by dissolving calculated quantity of ammonium metavanadate in hot double distilled water. The vanadium (V) solution was standardized against standard ferrous ammonium sulphate solution by using diphenylamine. Similarly the stock solution of sodium perchlorate was prepared by dissolving equivalent quantities of sodium carbonate and perchloric acid (70% E. Merck) in water to maintain ionic strength. Standard solutions of o-Me-PAAH, m-Me-PAAH and p-Me-PAAH were prepared by dissolving corresponding hydrazide in ethanol-water (60% + 40%) system. The double distilled water was used throughout the experiment.

The pseudo-first order condition was maintained throught the reaction in which concentration of hydrazide was in excess as compared to that of ammonium metavanadate. The formation of complex between vanadium (V) and hydrazide was found during the course of the reaction. The plot of the log of absorbance at 390 against time for each hydrazide was used to calculate the pseudo-first order rate constant k found to be fairly constant at different concentrations of vanadium (V). The UV-VIS. Spectrophotometer ELICO-(INDIA) S.L.159 was used to measure the absorbance of the reaction mixture at 390 spectrophotometrically.

Results and Discussion

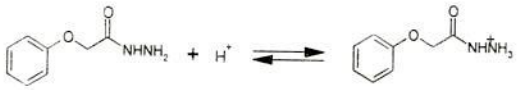
Effect of Concentration of Reactant: The formation of complex between vanadium (V) and hydrazide (Fig. 1) takes place during the course of the reaction. The specific rate of oxidation is independent of concentration of oxidant (Table 2) and hydrazide (Table 3).The order is unity with oxidant concentration. The specific rate of oxidation decreases with increase in concentration of hydrazide. The decrease in rate constant as the concentration of hydrazide increases can be attributed to greater stability of the complex in alcoholic medium probably due to solvation[16]. This is evident from initial absorbance values of the complex with different hydrazide concentrations.

Effect of Sulphuric Acid Concentration: As the concentration of acid increases, the specific reaction rate increases. This effect of sulphuric acid on the reaction may be due to the protonation prior equilibria. Oxidant vanadium (V) was reported to undergo variety of protonation reactions[2] and

under the present experimental conditions protonated vanadate might be considered as a predominant species as shown by equilibrium (1):

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \qquad K_1 (1)$$

The substrate, hydrazide is also known to undergo protonation[19] according to equilibrium (2):



K2 (2)

The protonation constants of both the oxidant and substrate, K_1 and K_2, are very high, thus converting both the reactants almost completely into their protonated forms in the hydrogen ion concentration range used in the present study (5.0×10^{-1} M to 5.0×10^{-2} M). Therefore, both the protonated forms of the reactants may be active in the present investigation. The graph of log k vs log [Acid] is linear and the order of reaction is found to be fractional (Fig. 2).

Effect of Ionic Strength, Dielectric Constant and Temperature: To study the effect of ionic strength, the concentration of sodium perchlorate in the reaction mixture was varied from 0.3×10^{-1} to 3.0×10^{-1} M. The evidence shows that increase in ionic strength has no influence on the rate of the reaction.

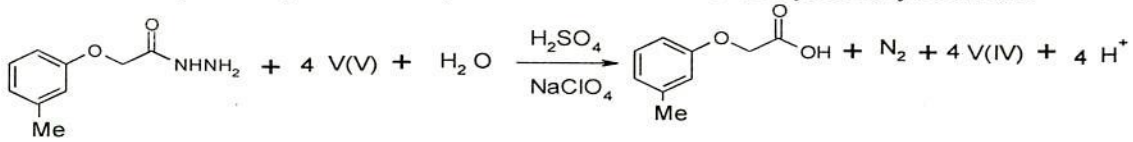
Various percentages of aqueous ethanol were used to investigate the effect of dielectric constant on specific rate of reaction which decreased with decrease in dielectric constant. The graphs of log k vs 1 /Dielectric Constant are plotted which are linear (Fig.3). Such decrease in rate with decrease in dielectric constant is reported[11].

The different temperatures ranges from 25° to 55°C were used to study the kinetics of oxidation of hydrazides. The log (Abs) against time plotted at different temperatures was found to be linear which reveals that the Pseudo-first order kinetic behavior of the reaction is not affected by change in temperature. The values of observed rate constants were used to determine various thermodynamic parameters like temperature coefficient, energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) (Table 1).

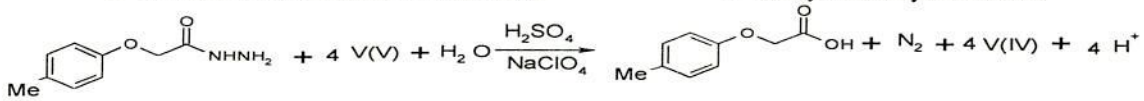
Reaction Intermediate, Stoichiomerty and Product Analysis: It is already seen that the order of the reaction with respect to vanadium (V) is one. The first order dependence of reaction rate on concentration of vanadium (V) itself indicates the possibility of formation of free radicals during the course of the reaction. The formation of free radicals or radical ions during the course of reaction was confirmed from induced polymerization of acrylonitrile[8]. The mole ratio of hydrazide: vanadium (V) is found to be 1:4 and it is independent of concentration of sulphuric acid that was used. The integral value of observed mole ratio, its independence on sulphuric acid concentration and formation of only carboxylic acid along with nitrogen gas, as oxidation product leads to deduce that the two rate determining steps occurring simultaneously result in the formation of one and the same intermediate. Although the observed mole ratio (substrate: oxidant) of the reaction is 1:4, as pointed out earlier, the order of reaction with respect to vanadium (V) is one. This fact makes it clear that three moles of vanadium (V) are consumed in fast step(s) taking place after rate determining step(s). Oxidation products identified in these reactions are given in scheme 1.

Scheme 1

o -Methyl Phenoxy Acetic acid Hydrazide — o -Methyl Phenoxy Acetic acid



m -Methyl Phenoxy Acetic acid Hydrazide — m -Methyl Phenoxy Acetic acid

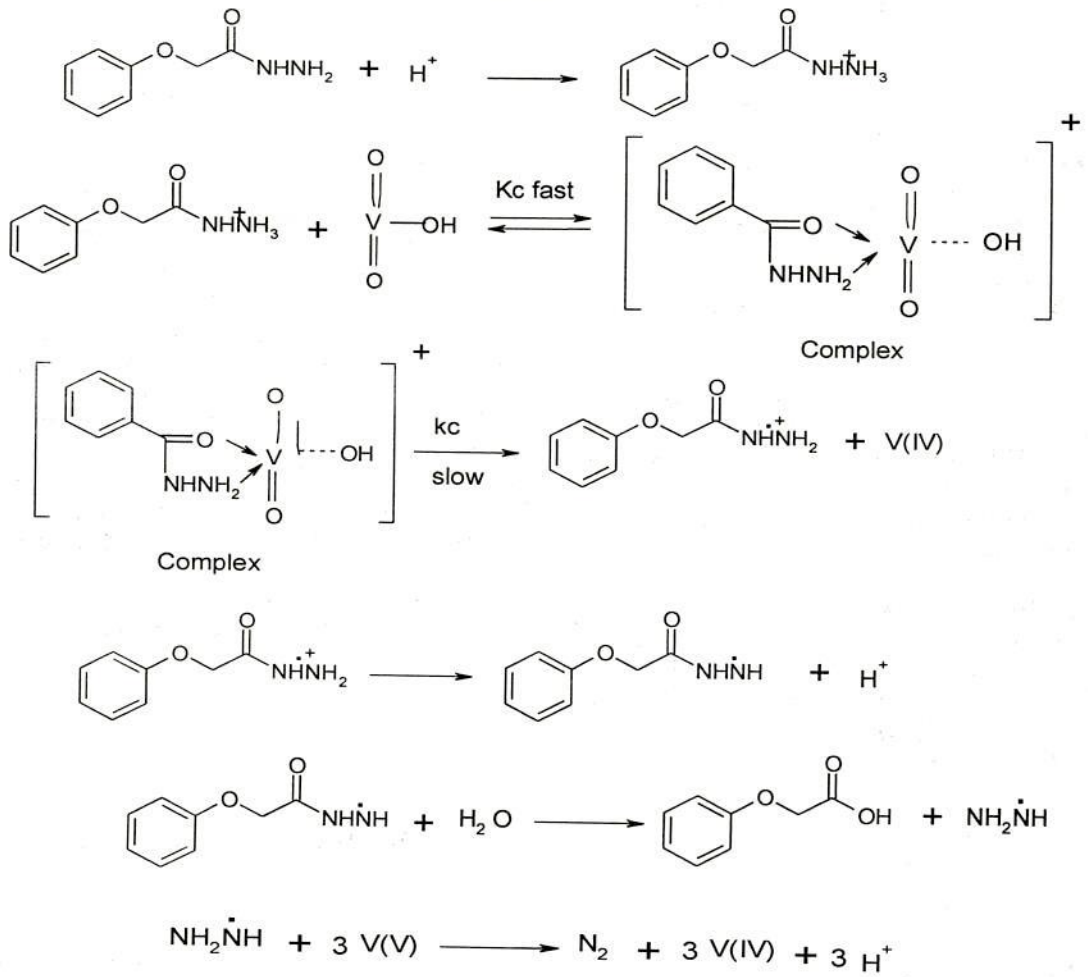


p-Methyl Phenoxy Acetic acid Hydrazide — p-Methyl Phenoxy Acetic acid

Besides the formation of corresponding aryloxy acetic acids, the nitrogen gas is also evolved in each reaction. The formation of carboxylic acids and N_2 in the oxidation of aliphatic as well as aromatic acid hydrazides[7] is well documented in chemical literature. The study of oxidation of hydrazide by different oxidants indicated that the formation of ammonia also takes place in addition to the formation of respective aryl oxy acetic acid and nitrogen[4,17].

The object of present study is to examine the effect of substituent's on the reaction rate. Hence it is essential to review the various mechanistic criteria usually employed in the determination of reaction mechanism and to suggest plausible mechanism on the basis of experimental facts. The mechanism in terms of the active species of the oxidant HVO_3 and substrate protonated hydrazide is shown in the scheme 2.

Scheme 2



According to the above scheme the rate of the reaction is given by:

Rate = k_c [Complex]

Substituting the value of [Complex] from the equilibrium,

Rate = $k_c K_c$ [HVO_3] [Ar-CoNHNH$_3$]

Conclusion

Relative reactivities of hydrazides: The objective of the present investigation is not only to develop method for the oxidation of hydrazides to their corresponding acids but to study the effect of position of same substituent in aromatic ring on the rate of reaction as well as mechanism.

The order of reactivities of the hydrazides under investigation is:

o-Me-PAAH < **m**-Me-PAAH < **p**-Me-PAAH.

In case of o-Me-PAAH the methyl group is nearer to reaction site and being more bulky and due to steric hindrance weak electron donating inductive effect might be operating which has negligible effect on its reactivity[14]. Alkyl groups were formerly regarded as electron donating

but many examples of behavior have been found that can be interrupted only by the conclusion that alkyl groups are electron withdrawing as compared to hydrogen. [13]

The slight increase in reaction rate in case of m-Me-PAAH and p-Me-PAAH is due to electron withdrawing inductive effect[14] of methyl group in comparison with hydrogen which can be attributed to similar observations comparatively as the reaction centre is away so the reaction rates are nearly constant.

Acknowledgement

Authors is very grateful to the Principal, Bharati Vidyapeeth's Matoshri Bayabai Shripatrao Kadam Kanya Mahavidyalaya Kadegaon, Dist. Sangli (M.S.) for providing the laboratory facilities to complete this investigation.

Table 1
Thermodynamic Parameters

	o-Me-PAAH	m-Me-PAAH	p-Me-PAAH
Ea (KJ mol^{-1})	55.22	56.60	56.73
$\Delta H^{\#}$ (KJ mol^{-1})	52.58	53.38	54.07
$\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	-141.68	-135.78	-134.86
$\Delta G^{\#}$ (KJ mol^{-1})	96.96	95.87	96.29

Table 2
Effect of [AMV] on the oxidation of hydrazides by vanadium (V)
[hydrazide] = 1.5 x 10^{-2} mol dm^{-3} [H_2SO_4] = 1.5 x 10^{-2} mol dm^{-3}
[$NaClO_4$] =1.1 x10^{-1} mol dm^{-3} Temp. = 35 ^{0} C λmax = 390nm

[AMV] x10^3 mol dm^{-3}	k x $10^4$$sec^{-1}$		
	o-Me-PAAH	m-Me-PAAH	p-Me-PAAH
0.3	3.03	3.65	3.76
0.6	3.11	3.68	3.84
1.2	2.99	3.61	3.72
1.5	2.92	3.49	3.65
1.8	2.70	3.57	3.68
2.4	2.84	3.42	3.53
3.0	2.80	3.49	3.60

Table 3
Effect of [hydrazide] on the oxidation of hydrazides by vanadium (V)
[AMV] = 1.5x 10^{-3} mol dm^{-3} [H_2SO_4] = 1.5 x 10^{-2} mol dm^{-3}
[$NaClO_4$] =1.1 x10^{-1} mol dm^{-3} Temp. = 35 ^{0} C, λmax = 390nm

[hydrazide] x10^2 mol dm^{-3}	k x $10^4$$sec^{-1}$		
	o-Me-PAAH	m-Me-PAAH	p-Me-PAAH
0.3	3.72	3.80	4.84
0.6	3.65	3.68	4.41
1.2	3.22	3.61	3.95
1.5	2.92	3.49	3.65
1.8	2.67	3.07	3.26
2.4	2.38	2.69	3.03
3.0	2.15	2.38	2.57

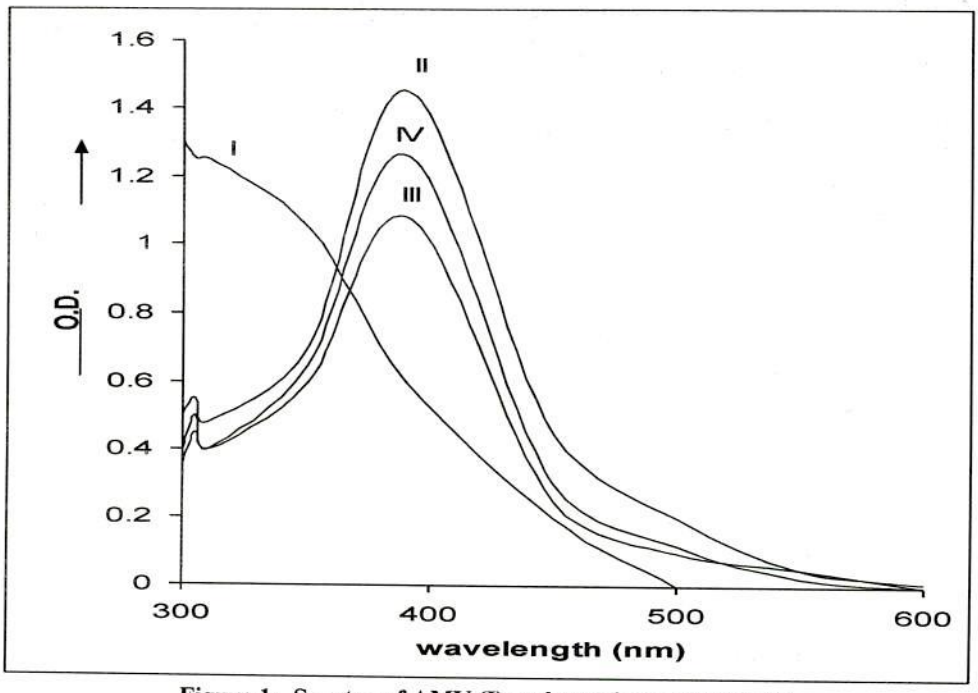


Figure 1: Spectra of AMV (I) and reaction mixture with o-Me- PAAH (II) m-Me-PAAH (III) and p-Me-PAAH (IV)
[hydrazide] = 1.5 x 10^{-3} mol dm^{-3}, [AMV] = 1.5x 10^{-3} mol dm^{-3}, [H_2SO_4] = 1.5 x 10^{-2} mol dm^{-3}, [$NaClO_4$] =1.1 x10^{-1} mol dm^{-3}, Temp. = 35 ^{0} C, λmax = 390nm

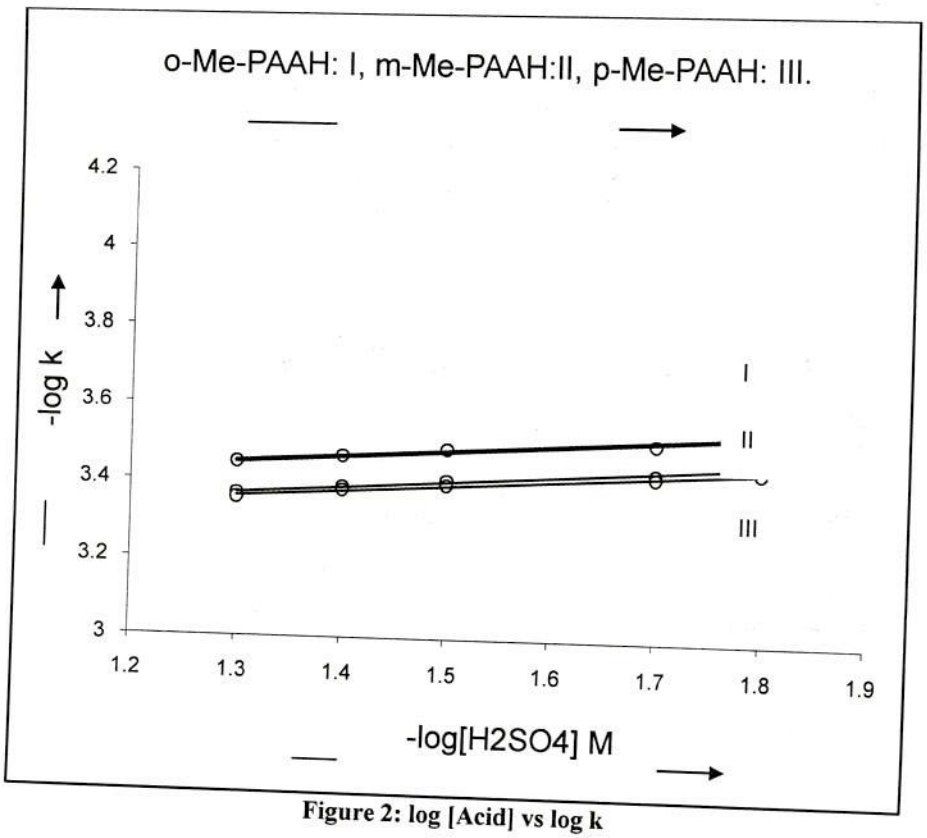


Figure 2: log [Acid] vs log k

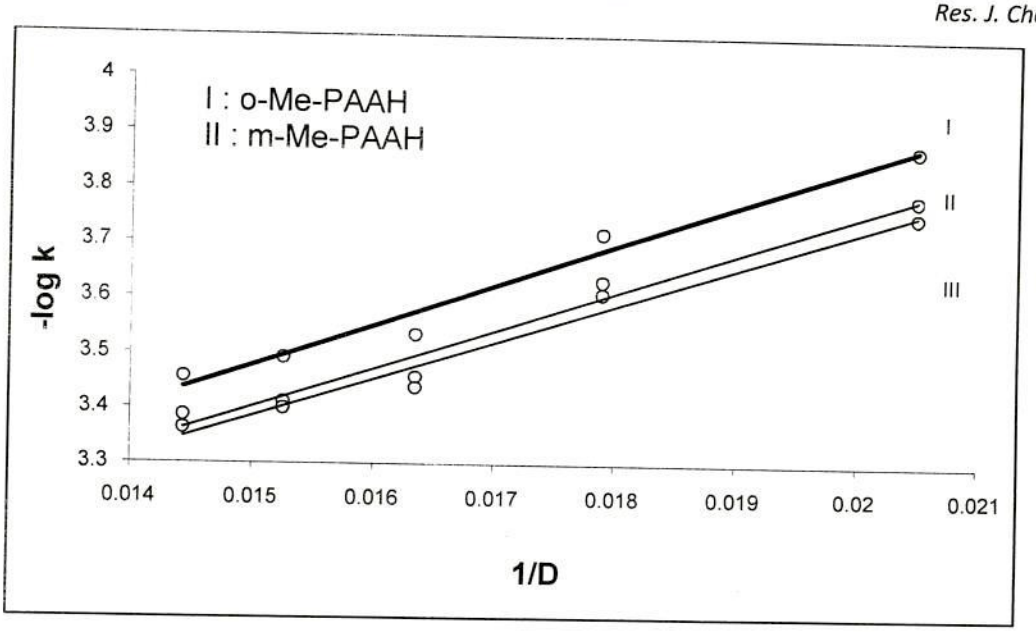


Figure 3: log k vs 1/D

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(Received 11th July 2014, accepted 16th September 2014)

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