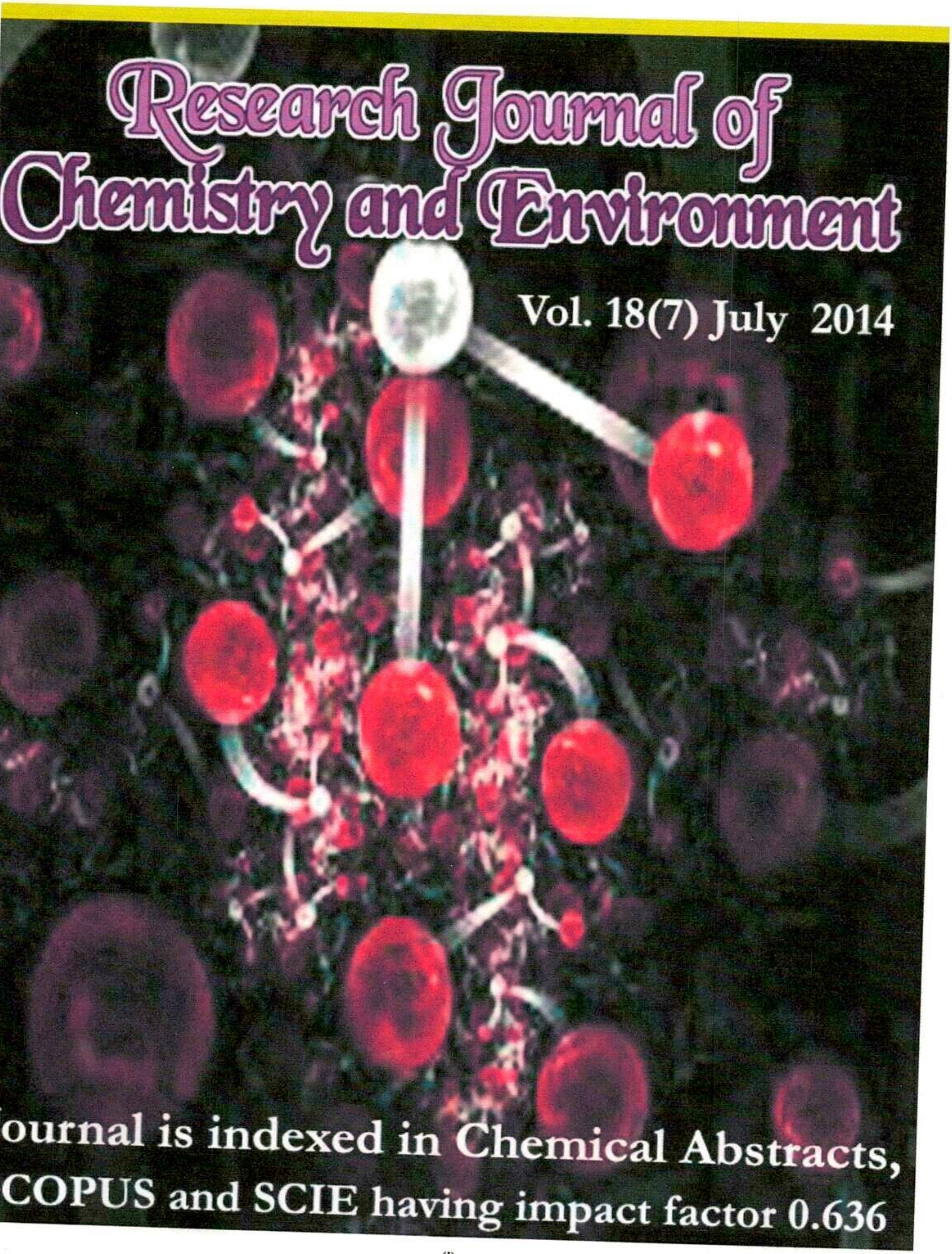

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CONTENTS

Effect of Substituent on Rate of Oxidation of Phenoxy Acetic Acid Hydrazides by Vanadium (V)

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Abstract

The reactions between vanadium (V) and phenoxy acetic acid hydrazide (PAAH), o-chloro phenoxy acetic acid hydrazide (o-Cl-PAAH) and p-chloro phenoxy acetic acid hydrazide (p-Cl-PAAH) were studied 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.($-\Delta S^{\#}$ = 155.98, 127.21 and 145.53 J K^{-1} mol^{-1} respective for PAAH, o-Cl-PAAH and p-Cl-PAAH respectively.)

Keywords: PAAH, o-Cl-PAAH, p-Cl-PAAH, hydrazides, pseudo-first order, vanadium (V).

Introduction

Chemical kinetics deals with the rate at which the chemical reactions take place and the influence of various factors such as concenteration, temperature, pressure catalysts etc. on the reaction rates. Different chemical reactions occur at different rates. Hydrazides are derivatives of carboxylic acids[9]. They have been extensively used in various fields of chemistry[3,6,10,12,21,22,23], therefore it is pertinent to understand the mechanism of their oxidation.

Material and Methods

PAAH, o-Cl-PAAH and p-Cl-PAAH were prepared by reported procedure[20]. The hydrazides were stored in ambere coloured bottles kept in dark place. Ammonium metavanadate, sulphuric acid and salt used were of AR grade. Double distilled water was used throughout the experiment. 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 PAAH, o-Cl-PAAH and p-Cl-PAAH solutions were prepared by dissolving corresponding hydrazide in ethanol-water (60% + 40%) system.

The reaction was studied under pseudo-first order condition in which concentration of hydrazide was in excess as compared to that of ammonium metavanadate. The reaction is found to proceed through formation of complex between vanadium (V) and hydrazide. The pseudo-first order rate constant k was obtained by plotting the log of absorbance at 390 against time for each hydrazide and was found to be fairly constant at different concentrations of vanadium (V). The progress of reaction was followed by measuring absorbance of the reaction mixture at 390 spectrophotometrically using UV-VIS. Spectrophotometer ELICO-(INDIA) S.L.159.

Results and Discussion

Effect of Reactant Concentration: The reaction is found to proceed through formation of complex between vanadium (V) and hydrazide (Fig. 1). 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: The specific reaction rate increases as the concentration of acid is increased. 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).

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \quad \text{--------------------} \quad K_1 \ (1)$$

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

$$\text{Ar-CONHNH}_2 + H^+ \rightleftharpoons \text{Ar-CONH}\overset{+}{\text{N}}\text{H}_3 \quad \text{---------} \quad K_2 \ (2)$$

The protonation constants of both 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 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: The effect of ionic strength was studied by varying the concentration of sodium perchlorate in the reaction mixture from 0.3×10^{-1} to 3.0×10^{-1} M. It is investigated that rate of reaction is not influenced by increase in ionic strength.

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

The kinetics of oxidation of hydrazides was studied at different temperatures ranging from 25° to 55°C. The log (Abs) against time plots at different temperatures are linear which reveal that the pseudo-first order kinetic behaviour 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).

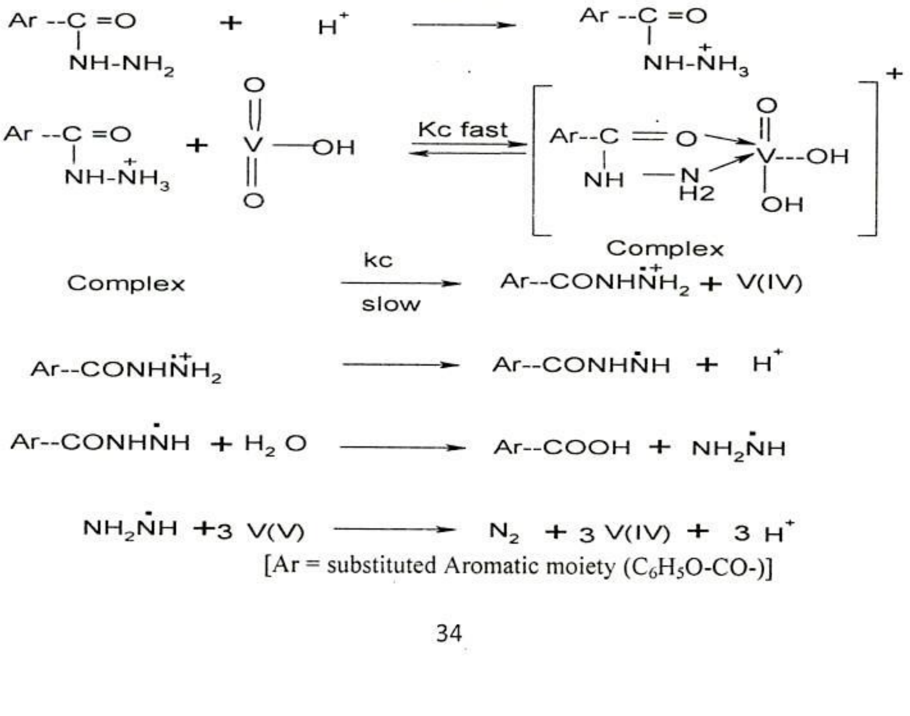
Reaction Intermediate, Stoichiomerty and Product Analysis: The formation of free radicals or radical ions during the course of reaction was confirmed from induced polymerisation of acrylonitrile[8]. The mole ratio of hydrazide: vanadium (V) is found to be 1:4 and it is independent of concentration of 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 led 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 3 moles of vanadium (V) are consumed in fast step(s) taking place after rate determining step(s).

The oxidation products identified in these reactions are as follows. Besides 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 as follows:

SCHEME



[Ar = substituted Aromatic moiety (C_6H_5O-CO-)]

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 order of reactivities of the hydrazides under investigation is PAAH < p-Cl- PAAH < o-Cl-PAAH. The higher rate of o-Cl-PAAH is due to strong electron withdrawing inductive effect[14] of chlorine which outweighs its weaker electron donating resonance effect because of distance in this process of oxidation. It is proved that field effects can be affected by solvent[1,13]. There might be some such stabilization induced by solvation[16] by ethanol. The comparative lower reactivity of oxidation of p-Cl-PAAH than o-Cl-PAAH can be attributed to weak electron withdrawing inductive effect of chlorine at p-position. The unsubstituted PAAH has lowest rate in above series of compounds under consideration.

Acknowledgement

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Table 1
Thermodynamic Parameters

	PAAH	o-Cl-PAAH	p-Cl-PAAH
Ea (KJ mol^{-1})	51.58	58.85	54.04
$\Delta H^{\#}$ (KJ mol^{-1})	49.02	56.30	50.70
$\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	-155.98	-127.21	-145.53
$\Delta G^{\#}$ (KJ mol^{-1})	97.84	96.13	96.25

Table 2
Effect of [AMV] on the oxidation of hydrazides by vanadium (V).
[hydrazide] = 1.5×10^{-2} mol dm^{-3}, $[H_2SO_4] = 1.5 \times 10^{-2}$ mol dm^{-3},
$[NaClO_4] = 1.0 \times 10^{-1}$ mol dm^{-3}, Temp. = 35^0 C, λmax = 393nm

[AMV] $\times 10^3$ mol dm^{-3}	**k x $10^4 sec^{-1}$**		
	PAAH	**o-Cl-PAAH**	**p-Cl-PAAH**
0.3	2.26	4.11	2.99
0.6	2.34	4.18	3.07
1.2	2.23	4.07	3.11
1.5	2.19	3.99	2.92
1.8	2.07	4.03	2.89
2.4	2.00	3.88	3.03
3.0	2.11	3.95	2.96

Table 3
Effect of [hydrazide] on the oxidation of hydrazides by vanadium (V)in 60% v/v ethanol.
[AMV] = 1.5×10^{-3} mol dm^{-3}, $[H_2SO_4] = 1.5 \times 10^{-2}$ mol dm^{-3},
$[NaClO_4] = 1.0 \times 10^{-1}$ mol dm^{-3}, Temp. = 35^0 C, λmax = 393nm

[hydrazide] $\times 10^2$ mol dm^{-3}	**k x $10^4 sec^{-1}$**		
	PAAH	**o-Cl-PAAH**	**p-Cl-PAAH**
0.3	3.65	7.72	4.03
0.6	3.37	5.49	3.72
1.2	2.96	4.76	3.26
1.5	2.19	3.99	2.92
1.8	2.11	3.72	2.67
2.4	1.73	3.11	2.46
3.0	1.38	2.73	2.26

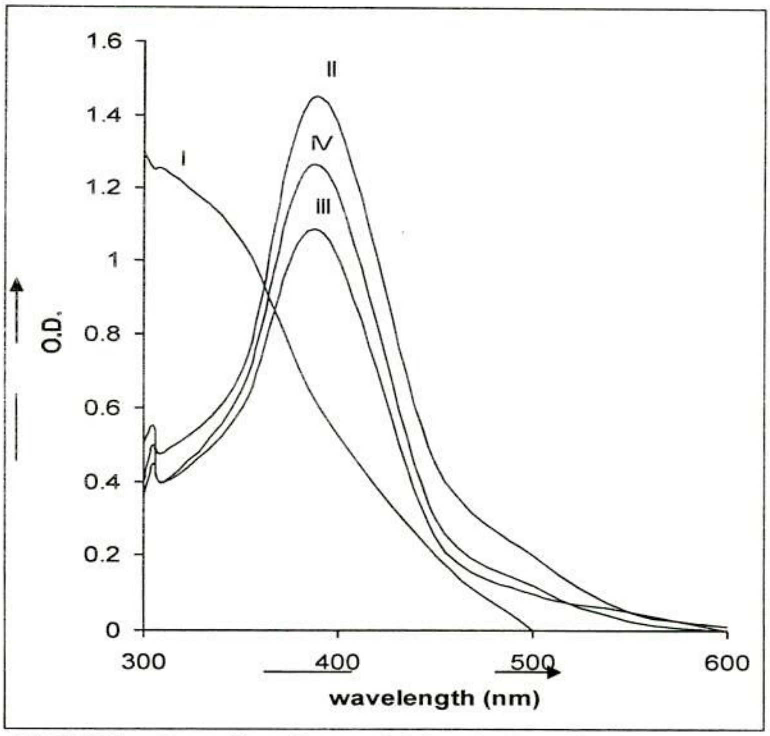

Figure 1: Spectra of AMV (I) and reaction mixture with PAAH (II), o-Cl-PAAH (III) and p-Cl-PAAH (IV)
[hydrazide] = 1.5×10^{-3} mol dm^{-3}, [AMV] = 1.5×10^{-3} mol dm^{-3}, [H_2SO_4] = 1.5×10^{-2} mol dm^{-3}, [$NaClO_4$] =1.0×10^{-1} mol dm^{-3}, Temp. = 35 ^{0} C, λmax = 393nm

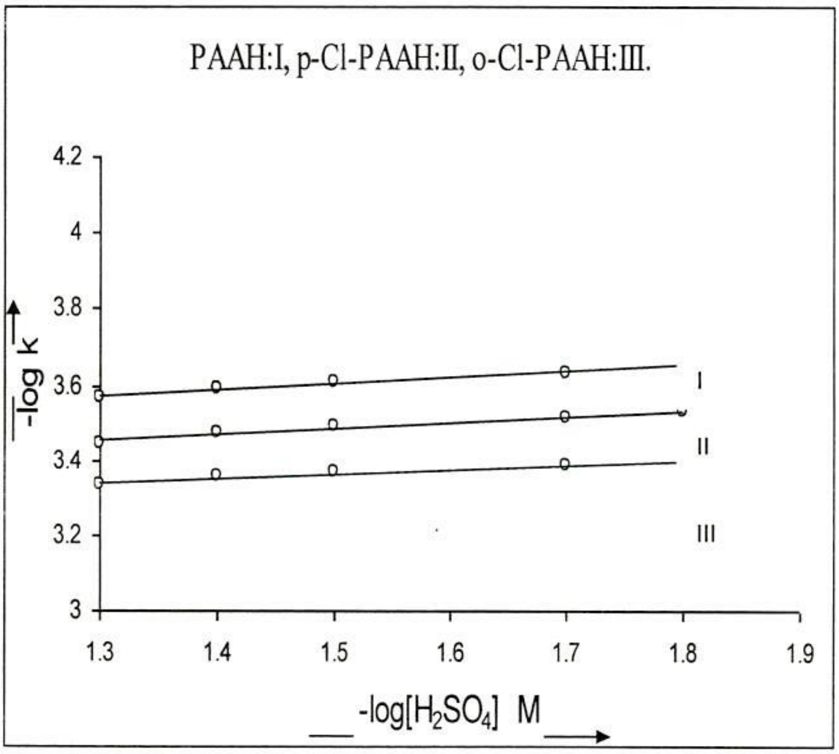

Figure 2: log [Acid] vs log k

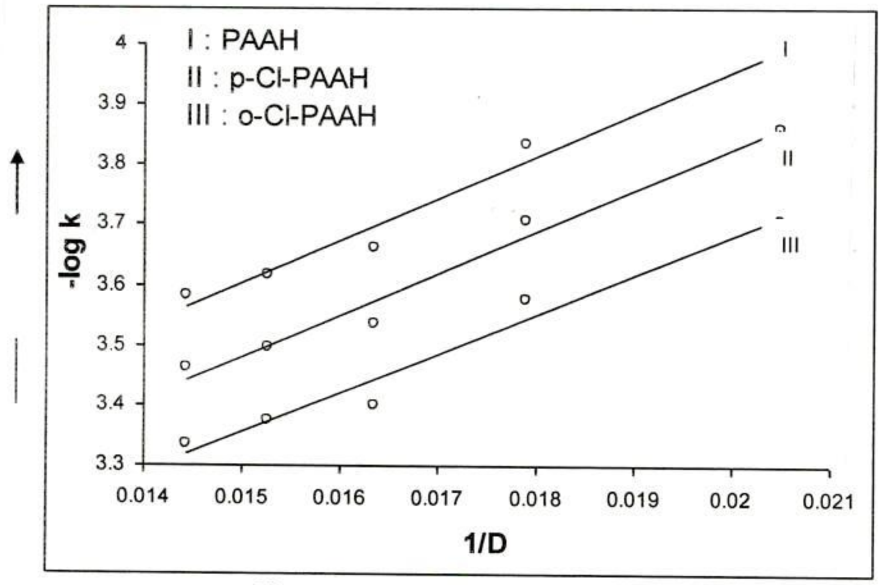

Figure 3: Effect of Dielectric Medium
[hydrazide] = 1.5 x 10^{-2} mol dm^{-3}, [AMV] = 1.5x 10^{-3} mol dm^{-3}, [H_2SO_4] = 1.5 x 10^{-2} mol dm^{-3}
[$NaClO_4$] =1.0 x10^{-1} mol dm^{-3}, Temp. = 35 ^{0} C, λmax =393 nm

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