

Research Article

Magnesium Monoperoxyphthalate Oxidation of Aromatic Anils in Aqueous Acetonitrile Medium

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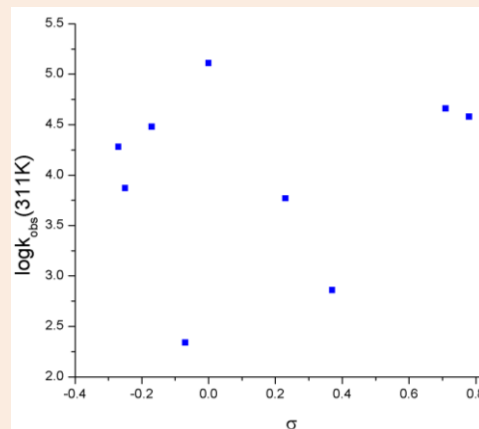
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Abstract

The magnesium monoperoxyphthalate (MMPP) oxidation of three meta- and five para- substituted aromatic anils in aqueous acetonitrile medium has been studied. The reaction followed second order kinetics with respect to the concentration of [Anil], and first order with respect to MMPP. The increase of $[H^+]$ in this oxidation retards the rate of the reaction. The added acrylonitrile has no effect on the reaction rate indicating the absence of free radical mechanism. The observed rate constant for the substituents were plotted against the Hammett constant, σ , and a concave upward curve was obtained for the anils with substituents in the benzaldehyde moiety. The electron withdrawing substituents fall on one side of the curve, having a negative ρ value and the electron releasing substituents fall on the other side, with a positive ρ value and a suitable mechanism was proposed.

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Introduction

Reactions using MMPP have been usually carried out in water or low molecular weight alcohols as solvents. For insoluble substrates in polar solvents, reactions have been conducted in biphasic media combined with a phase transfer catalyst. However, reactions in ethanol or phase transfer media are often not efficacious. An attempt to overcome these limitations has been the use of a solid-phase-supported version of MMPP on wet silica gel or moist alumina [1]. Among the oxygen donors, towards oxidation, MMPP was recently found to be a very efficient oxidant [2-5] In this paper, we report simple and effective approaches for the selective aromatic anils using MMPP in organic solvents. Aromatic anils, X-CH=N-Y have two phenyl rings X and Y, the ring X-originate from the aromatic benzaldehyde moiety and Y from aniline moiety. It is possible to evaluate the reaction constant (ρ) from the Hammett plot by varying the substituents in one of the rings X or Y, and keeping the same substituent in the other ring. It is therefore possible to get several reaction constants for different substituents in one of the two rings. The kinetics and mechanism of oxidation of some substituted anils, using several oxidants have been documented [6-9]. However, there is no study on the oxidation of *meta*- and *para*- substituted aromatic anils with MMPP in aqueous acetonitrile medium.

Experimental

Anils are prepared [9, 16] by refluxing equimolar quantities of benzaldehyde and aniline (Sigma Aldrich) in ethanol for about 2 to 3 h. The resulting solution is cooled and poured into cold water. The precipitated anil is filtered off, washed with ethanol and dried. It is recrystallised from ethanol. The anils is checked by determining their melting points and UV-VIS spectrum. All other chemicals and solvents were of analytical grade (Merck, India). All the

reagents are prepared just before the reactions are carried out. Aqueous solution of magnesium monoperoxyphthalate (Sigma Aldrich) is prepared fresh and standardized iodometrically. All the reactions are carried out in a thermostat and the temperature is controlled to $\pm 0.1^\circ\text{C}$. The reactions were carried out under pseudo-first order conditions by keeping an excess of anil over MMPP. The mixture is homogeneous throughout the course of the reaction. The progress of the reactions is followed by estimating the unreacted MMPP iodometrically at regular time intervals. The rate constants (k_{obs}) are from log (titre) versus time plots. Duplicate runs showed that the rate constants were reproducible to within $\pm 3\%$. Solutions of anil containing an excess of MMPP were kept overnight at room temperature. Titrimetric estimation of the concentration of MMPP consumed and assuming that all the anil taken had reacted, the stoichiometry of anil:MMPP was found to be 1:1. After 24h, the reaction mixture ethanol is extracted. The dark brown extract, when subjected to TLC, gives two distinct spots. On evaporation of ethanol the products are found to be benzaldehyde which is identified by the isolation of its 2,4-dinitrophenylhydrazone derivative and azobenzene identified by its m. p. and UV-VIS spectrum.

The oxidation reactions of *meta*- and *para*- substituents of aromatic anils are studied at different temperatures (296, 301, 306, 311 and 316K) to evaluate various thermodynamic parameters. From the Eyrings equation [10], the thermodynamic parameters, enthalpy of activation and entropy of activation are figured out from the expression

$$k_{\text{obs}} = (k_{\text{b}}T / h)\exp^{\Delta G^\ddagger / RT} \quad (1)$$

Where k_{b} is Boltzmann's constant, T is the temperature in Kelvin, h is plank's constant, R is the gas constant, ΔG^\ddagger is the activation of Gibbs free energy, ΔH^\ddagger is the enthalpy of activation and ΔS^\ddagger is the entropy of activation. ΔG^\ddagger and energy of activation (E_{a}) can be calculated from the following expressions respectively.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S \text{ and } E_{\text{a}} = \Delta H^\ddagger + RT \quad (2)$$

Results and Discussion

Effect of variation of substrate concentration

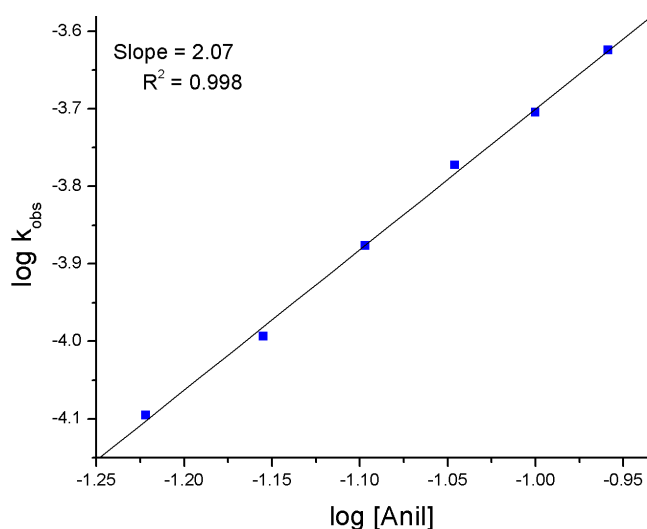


Figure 1 Plot of $\log k_{\text{obs}}$ vs $\log [\text{Anil}]$ for the oxidation of anil by MMPP. [oxidant] = 0.005M, acetonitrile:water = 60:40, $[\text{H}^+] = 0.2 \text{ N}$, temperature = 306 K

The increase in aromatic anil concentration increases the reaction rate at constant concentration of MMPP, H^+ and fixed percentage of acetonitrile. The slope of the plot is two. It reveals that the order of the reaction with respect to the [anil] is two, with a correlation coefficient $r = 0.998$ in Fig.1. The kinetic order in acidity appears to be united, but increase in $[\text{H}^+]$, decreases the rate of the reaction. The low dielectric constant of the medium facilitates the reactivity.

The ionic strength of the reaction varies by the addition of Na_2SO_4 and its influence on reaction rate is studied and it is found that it has no significant effect on the reactivity. Addition of Mn(II) decreases the rate of the reaction.

Effect of variation of H^+ concentration

The increase of hydrogen ion concentration decreases the rate of the reaction. The plot $\log k_{\text{obs}}$ versus $\log[\text{H}^+]$ gave a straight line in Fig.2.

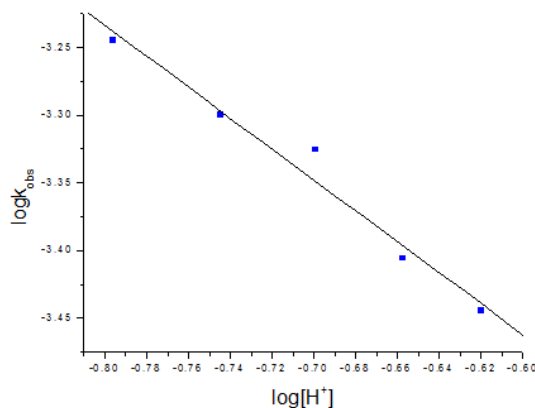


Figure 2 Plot of $\log k_{\text{obs}}$ vs $\log [\text{H}^+]$ for the oxidation of anil by MMPP. [oxidant] = 0.005M, acetonitrile:water = 60:40, $[\text{H}^+] = 0.2 \text{ N}$, temperature = 306 K

The experimental results represented that the increase of H^+ retards the rate of the reaction. With the decrease of H^+ , the molecules gains a proton, becomes less negatively charged and hence the rate of the reaction decreases [10].

Effect of variation in temperature

The oxidation of anil was studied at different temperatures 296-316 K maintaining the concentration of anil, MMPP, H^+ and acetonitrile. The plot of $\ln k_{\text{obs}} / T$ versus $1/T$ was found to be linear. The thermodynamic parameter ΔH^\ddagger was found to be linear. The thermodynamic parameter ΔH^\ddagger was found to be $224.18 \text{ KJ mol}^{-1}$, $\Delta S = 240.18 \text{ JK}^{-1}\text{mol}^{-1}$, $\Delta G^\ddagger = 298.27 \text{ KJ mol}^{-1}$ and $E_a = 226.67 \text{ mol}^{-1}\text{K}^{-1}$. The negative values of entropy of activation reveals that the intermediate is more firm than the initial state. Temperature dependence studies are conducted for all the substituted anils (substitution in X ring) between 296 and 316 K. The rate constants for the reaction systems and activation parameters are evaluated.

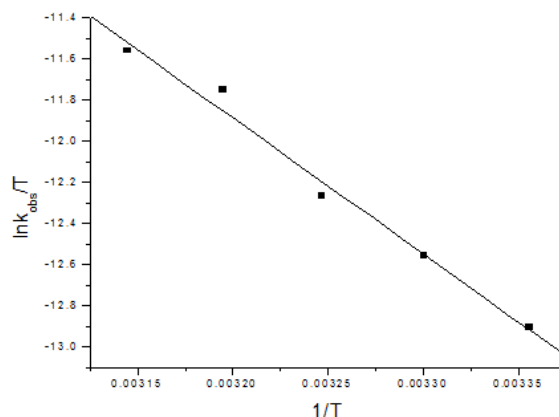


Figure 3 Plot of $\log k_{\text{obs}}/T$ vs $1/T$ for the oxidation of anil by MMPP. [oxidant] = 0.005M, acetonitrile:water = 60:40, $[\text{H}^+] = 0.2 \text{ N}$

Effect of dielectric constant

In order to determine the effect of dielectric constant of the medium on rate, the oxidation of anil by MMPP was studied in aqueous acetonitrile mixtures of different compositions. The results obtained (Table.1) shows that the rate increases with decrease in percentage of acetonitrile, i.e., with increasing dielectric constant, and leads to the influence that there is a charge development in the transition state involving a more polar activated complex than the reactants [11,12], suggesting a polar mechanism.

Table 1 Pseudo-first order rate constants for the oxidation of anils by MMPP in different acetonitrile compositions.

CH ₃ CN:H ₂ O	Dielectric constant (D)	10 ⁴ kobs(S ⁻¹)
90:10	41.47	1.35
80:20	45.48	1.82
70:30	49.71	2.09
60:40	53.83	2.41
50:50	57.95	2.96

$$[\text{Anil}] = 0.1 \text{ mol dm}^{-3}; [\text{MMPP}] = 0.005 \text{ mol dm}^{-3}$$

Test for free radical intermediates

No turbidity was observed when a freshly distilled acrylonitrile monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

Effect of Substituents on the Reaction Rate

The kinetics and oxidation of anil and H, *m*-CH₃, *p*-CH₃, *p*-OC₂H₅, *p*-OCH₃, *p*-Cl, *m*-Cl, *m*-NO₂ and *p*-NO₂ anils were conducted under pseudofirst order conditions at different temperatures to determine various thermodynamic parameters. ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and E_a were determined and tabulated (Table 2). The analysis of the data in the Table 2 indicate that the oxidation is neither isoenthalpic nor isoentropic but confirms with isokinetic relationship of compensation law. Since the reactions are of ion-polar, it is expected that the entropy of the activated complex for all the anils should be nearly the same order of magnitude. But due to the variation in polarity of different anils, ΔS^\ddagger may be different for different anils [13], as observed in the present findings. But the isokinetic relationship exists. The plot of activation enthalpy versus activation entropy follows a straight line as shown in the Fig.4. Isokinetic temperature is the temperature at which all the compounds of the series react equally fast and was determined from the following equation. $\Delta H^\ddagger = \Delta H^0 + \beta \Delta S^\ddagger$

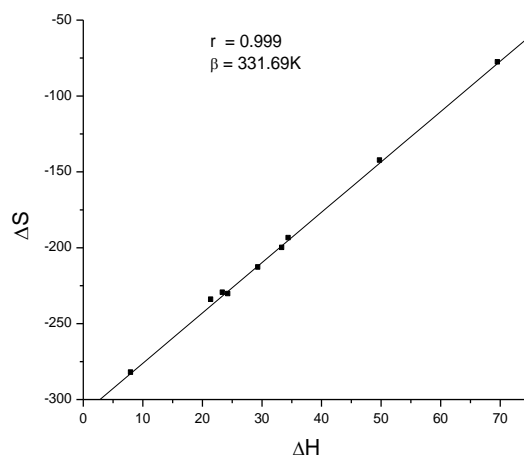


Figure 4 Isokinetic plot for the oxidation of anil by MMPP

Where β is the isokinetic temperature and it was found to be 331.69K which is greater than the experiment temperature. The function of isokinetic relationship reveals that a common mechanism is working in all the anil oxidation reactions.

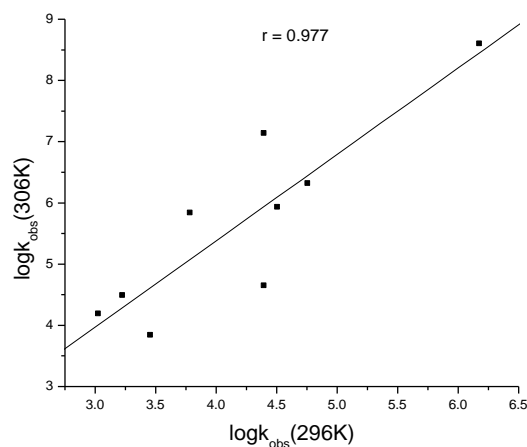


Figure 5 Exner plot for the oxidation of anil by MMPP

The values of free energy of activation of the reactions were found to be more or less similar. This is due to the fact that at isokinetic temperature the change of substituent has no influence on the free energy of activation.

If the isokinetic temperature is infinite in isoentropic oxidation reactions only the enthalpy of activation finalized the reactivity and if the isokinetic temperature is zero in isoenthalpic oxidation reactions only the entropy of activation finalized the reactivity [11]. However the Exner relationship (Fig.5), the linear logarithmic relationship between the rates at two temperatures, confirms the operation of a common mechanism throughout the series.

Table 2 Temperature effect and thermodynamic parameters of MMPP oxidation of anils.

Moie ty	S _c	N _o	Substituents	$10^{-4} \times k_{\text{obs}} (\text{s}^{-1})$					ΔH^{\ddagger} kJ mol ⁻¹	$-\Delta S^{\ddagger}$ J mol ⁻¹ K ⁻¹	ΔG^{\ddagger} kJ mol ⁻¹	E_a kJ mol ⁻¹ K ⁻¹	r	SD
				23°C	28°C	33°C	38°C	43°C						
benzaldehyde	1	H		1.56	1.70	1.94	2.28	3.03	224.18	240.18	298.27	226.67	0.991	0.05
	2	m-CH ₃		1.40	1.54	1.82	2.19	3.15	25.51	224.21	95.21	28.01	0.997	0.07
	3	p-CH ₃		1.71	2.05	2.89	3.88	4.87	39.07	180.51	94.13	40.25	0.995	0.03
	4	p-OC ₂ H ₅		1.27	1.39	1.62	2.06	3.39	31.62	204.29	96.26	34.12	0.982	0.12
	5	p-OCH ₃		2.95	3.31	4.64	5.41	5.07	20.09	236.37	94.43	22.23	0.985	0.10
	6	p-Cl		1.69	2.23	2.61	3.12	2.63	15.56	258.15	95.87	17.06	0.838	0.11
	7	m-Cl		1.19	1.33	1.78	2.01	3.56	36.93	193.20	96.74	36.71	0.974	0.13
	8	m-NO ₂		2.56	2.81	3.74	3.70	4.74	19.27	241.29	94.96	21.26	0.995	0.06
	9	p-NO ₂		1.71	2.84	3.48	5.59	5.96	101.15	25.34	93.93	102.32	0.998	0.49

[Anil] = 0.1 mol dm⁻³; [MMPP] = 0.005 mol dm⁻³; [H⁺] = 0.2 N; CH₃CN – H₂O = 60:40

Deviation from the Hammett Relationship

Hammett Plot for Benzaldehyde Moiety

The concave upward curve is obtained for the anils with substituents in benzaldehyde moiety (Figure 6). The electron-releasing substituents fall on the one side of the curve with a negative slope and the electron-withdrawing substituents on the other side with a positive slope. The isokinetic plot and Exner plot reveals that there is no change in the

reaction mechanism with respect to the substituents in benzaldehyde moiety. *meta*- and *para*- substituted anils with substituents in benzaldehyde moiety in aqueous acetonitrile at 296K – 316K confirm the Exner relationship, also the activation parameters to the isokinetic relationship but not to any of the linear free energy relationships. The isokinetic temperature is greater than the experimental range. The values of the negative and positive ρ values, ρ^+ and ρ^- , respectively, at different temperature are given in Table 3.

Table 3 Reaction constant for the MMPP oxidation of aromatic anils

Substituents	Temperature (K)	ρ^+	ρ^-
Benzaldehyde moiety	296	0.101	0.273
	301	0.127	0.049
	306	0.325	0.361
	311	0.889	1.027
	316	2.267	0.865

The unsubstituted anil is the most reactive in this series. Since the electron releasing substituents also retard the rate of the reaction, the rate-determining step proceeds with the development of negative charge on the nitrogen atom of anil. It is to be noted that this kind of transition state has been suggested in the oxidation of anil by PPMS [16]. Ramkrishnan Venkatesh and Kulandaivelu Karunakarn [16] have established the order dependence with respect to the reactants and other kinetic parameters of anils (substitution only in benzaldehyde moiety). The formation of oxalatochromate species is reported as the intermediate of the reaction since oxalic acid is used as catalyst.

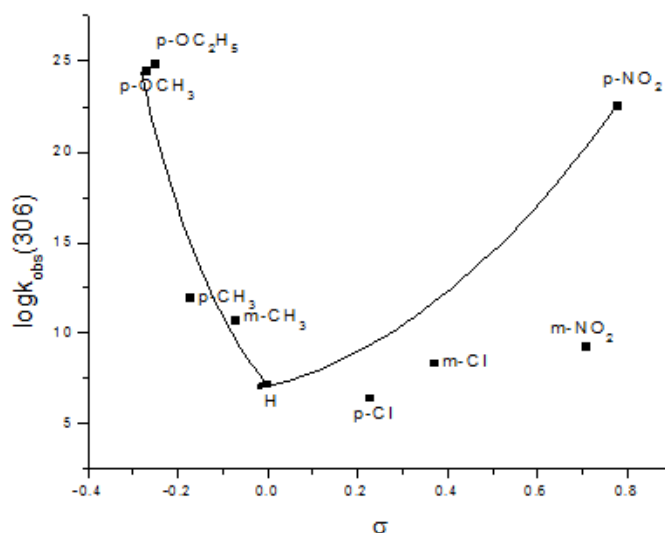


Figure 6 Hammett plot for MMPP oxidation of aromatic anils (substitution in benzaldehyde moiety) at 306K.

Structure – Reactivity Correlation

Negative entropy of activation also gives the information that the complex formed is an associate type with a greater degree of charge in transition state than initial state [14]. The rate data obtained is also unsuccessful in proving that the typical Hammett equation $\log k_{\text{obs}}$ vs σ is a dispersed gram and a sensitive plot (Fig.7) at the temperatures studied. The correlation coefficient (r) of the dispersed gram is found to be 0.078 with standard deviation of 1.271.

Literature study [17] also reveals that correlation obtained with it are poor as the substituents are conjugated with the reaction centre, where the problem arose with anilinium ions, where a lone pair of electrons on the NH_2 group can be delocalized into substituents such as *p*- NO_2 . The correlation of oxidation rates of *meta*- and *para*- substituted anils are correlated separately with any of the unit parameters (*meta*: σ , σ_m^+ ; *para*: σ , σ_p^+ , σ_p^-) was also found to be

ineffective. The oxidation rates measured at 296, 301, 306, 311 and 316K were analysed in terms of dual substituent parameter equations (*meta*: σ_I , σ_R ; σ_I , σ_R^- ; σ_I , σ_R^+ ; F, R; *para*: σ_I , σ_R ; σ_I , σ_R^- ; σ_I , σ_R^+ ; F, R) was also found to be unsuccessful.

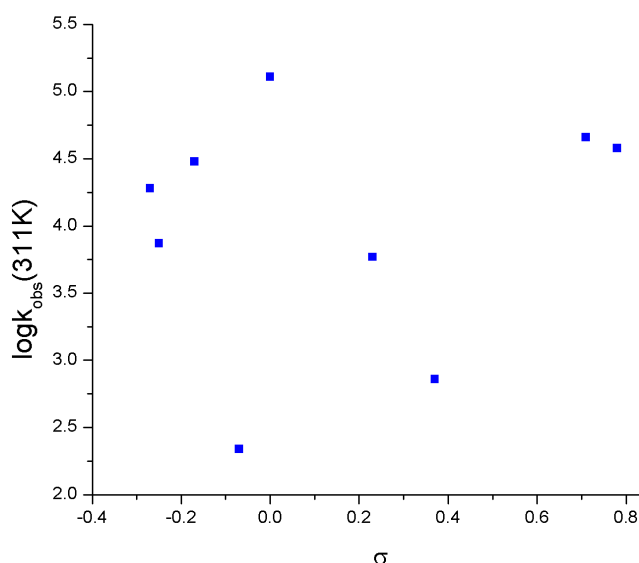


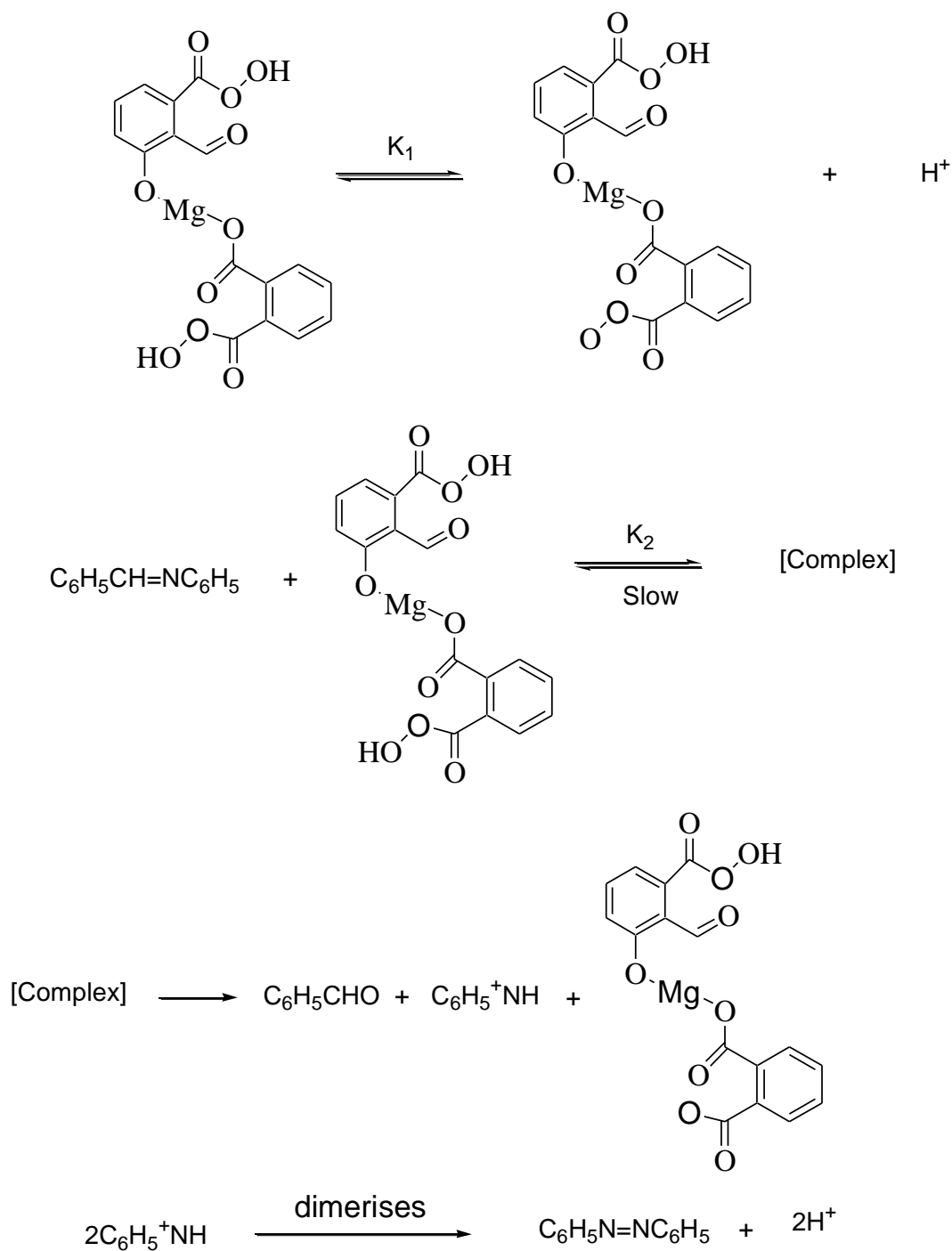
Figure 7 Hammett plot for the oxidation of anilins by MMPP

The possible reason for the lack of free energy relationship is the isokinetic temperature 331.6 K which is greater than the experimental temperature. The same type of results was also reported by Elango and Buvanewari [18]. Operation of inductive and resonance effect opposing each other is known but the present study has no parallel [14]. The less pronounced substituent can be explained only by the compensation effect. The influence of the substituents on the reactivity of the nucleophile is approximately compensated by the influence of the same substituent on the reactivity of the electrophile [19]. In some of the substituted anil exact compensation is doubtful and the resultant effect is experienced on the oxidation rate.

Mechanism

The addition of acrylonitrile monomer showed no variation in the reaction rate and no formation of turbidity in the oxidation of substituted aromatic anils. Furthermore, the rate of conversion is invariant when acrylonitrile is added. This rules out the presence of free radical mechanism in this oxidation reaction. So the ionic reaction is preferred in this oxidation study. Generally, the enhancement of the electrophilic activity of peroxide will minimize the importance of undesirable free radical pathways, resulting in a mixture of products [15]. Usually peroxy ions act as strong nucleophiles. The absorption spectra represent spectral changes supporting the complex formation. The investigation results illustrate a fascinating note that the increase of H^+ retards the rate of the reaction.

With the decrease of pH, the molecule gains a proton, becomes less negatively charged and hence the rate of the reaction decreases [10]. Also in strong acid, the anil exists as $\text{C}_6\text{H}_5\text{CH}=\text{NHC}_6\text{H}_5$ form. It is observed that when the acid strength is increased, there is a decrease in the rate which may be due to the less reactive protonated form than non-protonated form. Based on the stoichiometry of the reaction and above experimental results, the following reactions (scheme 1) are believed to constitute the most probable mechanism of the reaction. The formation of complex is in agreement with the literature study [6, 15] and the intermediate formed is experimentally confirmed at 790nm. The next step (decomposition of complex) is a slow reaction and is likely to be the rate determining step. Simultaneously, at 429nm, a peak appears and is stable till the end of the reaction, which is the azobenzene product. Based on the above experimental observations, a probable mechanism, shown in Scheme 1 is suggested.



Scheme 1 Probable mechanism for the oxidation of aromatic anil by MMPP

The above mechanism leads to the following rate law:

$$\text{Rate} = -d[\text{MMPP}] / dt = K_1 k_2 [\text{anil}] [\text{MMPP}]$$

This rate law satisfactory explains all the experimental results.

Conclusion

The oxidation of aromatic anils by MMPP is the second order with respect to [anil] and is the first order with respect to MMPP under the experimental conditions, and the aromatic anil is oxidized to benzaldehyde and azobenzene. The addition of H⁺ retards the rate of the reaction shows that the protonated anil was less reactive in this oxidation reaction. Concave upward curve is observed for the substituents in the benzaldehyde moiety. The correlations of oxidation rates substituted anils are correlated separately with any of the unit parameters which is also found to be ineffective. The oxidation rates analysed in terms of dual substituent parameter equations is also found to be unsuccessful. Solvent interaction also plays an important role in leading the reactivity. The formation of charged intermediate compound was supported by the high negative values of entropy of activation and a most probable mechanism has been proposed for oxidation of anils by MMPP. With MMPP as oxygen donor, was proved to be a more effective oxidant in anil.

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