

Oxidation of Aromatic Anils by Sodium Perborate in Aqueous Acetic Acid Medium

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The kinetics of oxidation of 9 *meta*- and 15 *para*- substituted aromatic anils by sodium perborate were investigated in aqueous acetic acid medium. The reaction was second order with respect to aromatic anil and first order with respect to the sodium perborate. The increase of $[H^+]$ in this oxidation retards the rate of the reaction. The observed rate constant for the substituents were plotted against the Hammett constant, σ and a non-linear concave downward curve was obtained for the anils with substituents in the aniline moiety. The observed break in the $\log k_{obs}$ versus σ was attributed to the transition state whereas the non-linear concave upward curve was observed for the substituents in the benzaldehyde moiety and a non-linear concave upward curve was observed for the substituents in the combination of aniline and 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.

Keywords: Aromatic anils, Kinetics, Oxidation, Sodium perborate.

INTRODUCTION

Sodium perborate (SPB, $NaBO_3 \cdot 4H_2O$), a peroxy salt of anionic formula $B_2(O)_2(OH)_4^{2-}$, is an inexpensive, innocuous, industrial chemical, extensively used in detergents as a bleaching agent¹. In aqueous solution it yields hydrogen peroxide and kinetic studies on sodium perborate oxidation in aqueous and partly aqueous media confirm the same²⁻⁷. In glacial acetic acid it is a highly effective reagent, the oxidant of choice⁸⁻¹⁰ and oxidizes anilines to azobenzenes, used in the manufacture of azo dyes, in good yield^{11,12}. Sodium perborate is a low cost and widely used industrial chemical. However, its utilization in organic synthesis has not received much attention. There have only been a few reported reactions using it as an oxidant, such as the cleavage of 1,2-diketones¹³, the oxidation of alkenylboronic acids¹⁴, the oxidations of anilines to azo compounds or nitroarenes and sulfides to sulfoxides or sulfones^{15,16}. The epoxidation by use of sodium perborate was also reported, but it was limited only to quinones¹⁷. Herein, we would like to report the oxidations of aromatic anils using sodium perborate.

EXPERIMENTAL

Anils were prepared¹⁸ by refluxing equimolar quantities of benzaldehyde and aniline (Sigma Aldrich) in ethanol for *ca.* 2-3 h. The resulting solution was cooled and poured into cold water. The precipitated anil was filtered off, washed with ethanol and dried. It was recrystallized from ethanol. The

purity of the anils was checked by determining their melting points and FT-IR spectrum. All other chemicals used were of analytical grade (Merck, India). Acetic acid was purified by redistillation. All the reagents were prepared just before the reactions were carried out. A solution of sodium perborate in acetic acid was prepared fresh and standardized iodometrically. All the reactions were carried out in a thermostat and the temperature was controlled to ± 0.1 °C. The reactions were performed under pseudo-first order conditions by maintain excess of anil over oxidant. The mixture was homogeneous throughout the course of the reaction. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically at regular time intervals. The rate constants (k_{obs}) were from \log (titre) versus time plots. All the rate constants were averages of two or more determinations.

Stoichiometry and product analysis: Under kinetic conditions, stoichiometric amounts of the substrate and sodium perborate were mixed. The reaction mixture ethanol was extracted. The dark brown extract, when subjected to TLC, gave two distinct spots. On evaporation of ethanol the products were found to be benzaldehyde which was confirmed by the isolation of its 2,4-dinitrophenylhydrazone derivative and azobenzene identified by its m.p. and UV-visible spectrum. Formation of the azobenzene was also confirmed by UV-visible spectra [λ_{max} 429 nm] of the reaction solutions during and after the completion of the reaction. This was in agreement with the literature value¹⁹. The λ_{max} of azobenzene was confirmed

by comparing with that of the authentic sample in aqueous acetic acid medium.

RESULTS AND DISCUSSION

The reaction followed second order kinetics with respect to the concentration of anil and is the first order with respect to the concentration of sodium perborate, respectively.

Under the identical experimental conditions $[Anil] \gg [SPB]$, the pseudo-first order linear plot of $\log(\text{titre})$ versus time is linear up to 80 %, depicted in Fig. 1. The order in $[anil]$ was two, as revealed by the slope of the plot of $\log k_{obs}$ against $\log [Anil]$ (Fig. 2), with correlation coefficient ($r = 0.992$). The kinetic order in acidity appears to be unity, but increase in $[H^+]$, the rate of the reaction was decreased.

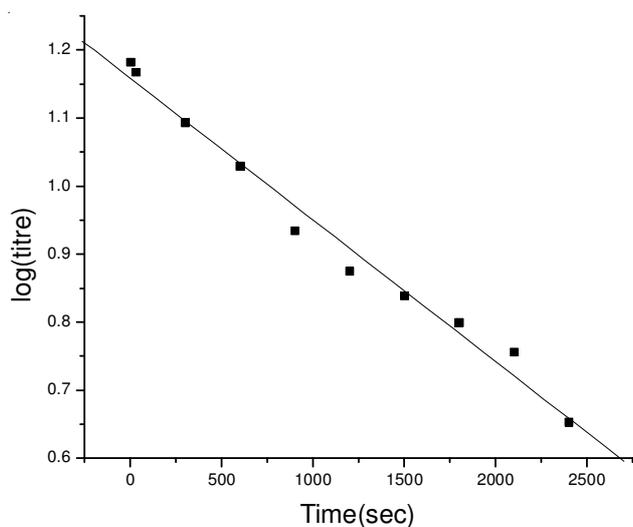


Fig. 1. Pseudo-first order plot for sodium perborate oxidation of aromatic anil at 308 K

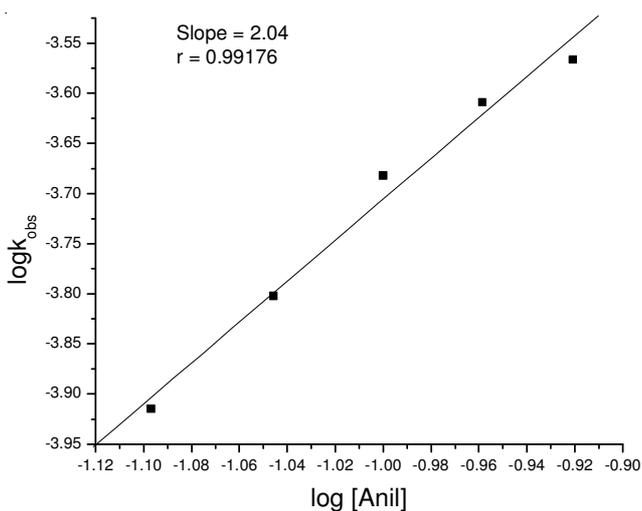


Fig. 2. Plot of $\log k_{obs}$ versus $\log [Anil]$ at 308 K

The kinetic results are summarized in Table-1. The ionic strength of the reaction varies by the addition of Na_2SO_4 and its influence on reaction rate was studied and has been found that it has no significant effect on the reactivity. No polymerization with acrylonitrile was observed. Addition of $Mn(II)$ decreases the rate of the reaction and the rate data are listed in

TABLE-1
EFFECT OF VARYING THE CONCENTRATION
OF ANIL, SPB AND H^+ ON THE RATE AT 308 K

$10^2 [Anil]$ (mol dm ⁻³)	$10^3 [SPB]$ (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	HOAc (%)	$10^4 k_{obs}$ (s ⁻¹)
8.0	5.0	1.0	50	1.21
9.0	5.0	1.0	50	1.57
10.0	5.0	1.0	50	2.07
11.0	5.0	1.0	50	2.46
12.0	5.0	1.0	50	2.71
10.0	3.0	1.0	50	1.56
10.0	4.0	1.0	50	1.84
10.0	5.0	1.0	50	2.07
10.0	6.0	1.0	50	1.78
10.0	7.0	1.0	50	1.56
10.0	5.0	0.8	50	2.68
10.0	5.0	0.9	50	2.18
10.0	5.0	1.0	50	2.07
10.0	5.0	1.1	50	1.51
10.0	5.0	1.2	50	1.33

Table-2. Temperature dependence studies were conducted for all the substituted anils (substitution in X and Y ring separately) between 298 and 318 K. The rate constants for the reaction systems and various thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger and E_a were found and tabulated (Table-3). When an attempt is made to fit in the rate data of *meta*- and *para*- substituted anils (substitution in aniline moiety and substitution in benzaldehyde moiety separately and substitution in both aniline moiety and benzaldehyde moiety) into the Hammett equation, a non-linear concave downward curve was obtained for the anils with substituents in the aniline moiety, whereas the non-linear concave upward curve was observed for the substituents in benzaldehyde moiety and a non-linear concave upward curve was observed for the substituents in the combination of aniline and benzaldehyde moiety.

TABLE-2
EFFECT OF $[Mn(II)]$, $[ACRYLONITRILE]$ AND
 $[Na_2SO_4]$ ON THE REACTION RATE AT 308 K

$[Mn(II)]$ (mol dm ⁻³)	$[Acrylonitrile]$ (mol dm ⁻³)	$[Na_2SO_4]$ (mol dm ⁻³)	$10^4 k_{obs}$ (s ⁻¹)
0	—	—	2.07
0.02	—	—	1.31
0.04	—	—	1.04
0.06	—	—	1.19
0.08	—	—	1.17
—	0	—	2.07
—	0.02	—	1.95
—	0.04	—	1.63
—	0.06	—	1.72
—	0.08	—	1.57
—	—	0	2.07
—	—	0.02	1.98
—	—	0.04	1.97
—	—	0.06	1.73
—	—	0.08	1.64

$[Anil] = 0.08 \text{ mol dm}^{-3}$; $[SPB] = 0.005 \text{ mol dm}^{-3}$; $[H^+] = 1.0 \text{ mol dm}^{-3}$,
HOAc-H₂O = 50 % (v/v); temperature = 308 K.

Effect of dielectric constant: The effect of solvent on the reaction rate was studied by varying the composition of acetic acid from 30-70 % (Table-4). The oxidations were carried out by maintaining the concentration of anils, sodium

TABLE-3
TEMPERATURE EFFECT AND THERMODYNAMIC PARAMETERS OF OXIDATION OF ANILS BY SPB IN ACETIC ACID

Moiety	S. No.	Substituents	$10^4 k_{\text{obs}} (\text{s}^{-1})$					ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	E_a (kJ mol ⁻¹ K ⁻¹)	r	SD
			25 °C	30 °C	35 °C	40 °C	45 °C						
Aniline	1	H	1.41	1.72	2.07	3.41	5.11	48.49	156.93	96.82	50.87	0.973	0.13
	2	<i>m</i> -CH ₃	1.30	1.60	1.97	2.18	2.82	26.63	230.03	97.48	29.01	0.993	0.04
	3	<i>p</i> -CH ₃	0.48	0.71	1.08	2.12	2.46	65.72	107.29	98.77	68.10	0.987	0.13
	4	<i>p</i> -OC ₂ H ₅	0.59	0.93	1.29	1.81	2.04	47.12	167.24	98.63	49.5	0.984	0.10
	5	<i>p</i> -OCH ₃	0.27	0.61	0.83	1.37	1.67	67.69	103.95	99.71	70.07	0.977	0.17
	6	<i>p</i> -Cl	1.49	1.92	2.48	2.87	3.35	29.40	219.39	96.97	31.78	0.992	0.04
	7	<i>m</i> -Cl	1.23	1.59	1.75	2.21	2.98	30.35	218.13	97.53	32.73	0.984	0.06
	8	<i>m</i> -NO ₂	2.22	2.70	3.42	4.26	5.13	30.91	211.33	95.99	33.29	0.999	0.01
	9	<i>p</i> -NO ₂	0.36	0.77	1.12	2.16	2.50	74.86	77.88	98.85	77.24	0.982	0.16
Benzaldehyde	1	H	1.41	1.72	2.07	3.41	5.11	48.49	156.93	96.82	50.87	0.973	0.13
	2	<i>m</i> -CH ₃	1.57	1.76	2.21	2.65	3.17	26.35	229.81	97.13	28.73	0.990	0.04
	3	<i>p</i> -CH ₃	1.94	2.27	3.12	4.21	5.31	38.75	186.49	96.18	41.13	0.993	0.05
	4	<i>p</i> -OC ₂ H ₅	1.52	2.28	2.74	3.41	4.55	38.33	189.11	96.58	40.71	0.991	0.06
	5	<i>p</i> -OCH ₃	2.29	2.61	3.18	3.57	4.28	15.80	258.08	95.29	18.18	0.944	0.06
	6	<i>p</i> -Cl	1.92	2.45	2.83	3.35	3.75	23.52	237.02	96.52	25.90	0.991	0.04
	7	<i>m</i> -Cl	1.37	1.78	2.06	2.65	3.29	31.29	213.99	96.89	33.67	0.997	0.03
	8	<i>m</i> -NO ₂	2.71	3.05	3.97	4.14	4.98	21.42	241.48	95.80	23.80	0.979	0.05
	9	<i>p</i> -NO ₂	2.43	2.85	3.35	5.11	5.62	32.95	204.06	95.80	35.33	0.974	0.09
Both in aniline and benzaldehyde	1	H	1.41	1.72	2.07	3.41	5.11	48.49	156.93	96.82	50.87	0.973	0.13
	2	<i>m</i> -CH ₃	1.34	1.69	1.89	2.03	2.34	18.00	258.41	97.59	20.38	0.977	0.04
	3	<i>p</i> -CH ₃	1.63	2.78	3.26	4.10	4.48	35.52	197.20	96.26	37.90	0.951	0.13
	4	<i>p</i> -OC ₂ H ₅	1.46	1.77	2.91	3.56	3.87	39.25	186.69	96.75	41.63	0.969	0.12
	5	<i>p</i> -OCH ₃	2.29	2.61	3.08	3.57	4.28	21.95	241.22	96.24	24.33	0.997	0.02
	6	<i>p</i> -Cl	1.23	1.57	2.96	3.45	3.77	45.20	167.92	96.92	47.58	0.954	0.16
	7	<i>m</i> -Cl	1.34	1.63	1.95	2.27	2.86	26.39	230.64	97.43	28.77	0.997	0.02
	8	<i>m</i> -NO ₂	1.90	2.55	3.86	4.08	4.66	33.31	203.96	96.13	35.69	0.957	0.12
	9	<i>p</i> -NO ₂	1.47	1.93	3.24	3.59	4.58	43.03	173.80	96.56	45.41	0.978	0.11

[Anil] = 0.1 mol dm⁻³, [SPB] = 0.005 mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, HOAc-H₂O = 50 % (v/v).

TABLE-4
PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE OXIDATION OF ANILS BY SPB IN DIFFERENT ACETIC ACID COMPOSITIONS

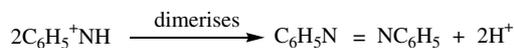
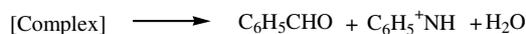
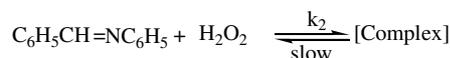
Acetic acid (%)	Dielectric constant (D)	$10^4 k_{\text{obs}} (\text{s}^{-1})$
30	56.83	2.84
40	49.60	2.59
50	42.37	2.07
60	35.14	1.80
70	27.90	1.37

[Anil] = 0.1 mol dm⁻³, [SPB] = 0.005 mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, temp. = 308 K.

perborate and temperature constant. The above observation clearly reveals that the rate decreases with increase in percentage of acetic acid, *i.e.*, with decreasing dielectric constant (D) or polarity of the medium. This directs to the conclusion that there is a charge development in the intermediate state involving a more polar intermediate than reactants, suggesting a polar (ionic) mechanism.

Mechanism: The addition of acrylonitrile monomer showed no variation in the reaction rate and no formation of turbidity in the oxidation of aromatic anils. This rules out the presence of free radical mechanism in this oxidation reaction. So the ionic reaction was 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 products²⁰. The investigation results illustrate a fascinating note that increase of H⁺ retards the rate of the reaction.

In crystalline state sodium perborate exists as a dimer with anionic formula B₂(O₂)₂(OH)₄²⁻. But in aqueous solution it affords H₂O₂. Although perboric acid is reported to exist in equilibrium with H₂O₂. Based on the stoichiometry of the reaction and above experimental results the following reactions (**Scheme-I**) are believed to constitute the most possible mechanism of the reaction.



Scheme-I: Probable mechanism for the oxidation of aromatic anil by sodium perborate

The formation of complex is in agreement with the literature study^{21,22} and the intermediate formed is experimentally confirmed at 790 nm. Decomposition of complex is a slow reaction and is likely to be the rate determining step. Simultaneously, at 429 nm, 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-I** is suggested.

The above mechanism leads to the following rate law:

$$\text{Rate} = \frac{d[\text{SPB}]}{dt} = K_1 k_2 [\text{Anil}][\text{SPB}]$$

This rate law satisfactory explains all the experimental results.

Effect of substituents on the reaction rate: The kinetics and oxidation of anil and *m*-CH₃, *p*-CH₃, *p*-OC₂H₅, *p*-OCH₃, *p*-Cl, *m*-Cl, *m*-NO₂, *p*-NO₂ anils were conducted under pseudo-first order conditions at five different temperatures 298, 303, 308, 313 and 318 K to determine various thermodynamics parameters. The analysis of the data in the Table-3 indicates that the oxidation is neither isoenthalpic nor isentropic 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. The effect of substituents on the rate was studied by varying the substituents H, *m*-CH₃, *p*-CH₃, *p*-OC₂H₅, *p*-OCH₃, *p*-Cl, *m*-Cl, *m*-NO₂ and *p*-NO₂ in one of the rings benzaldehyde (or) aniline.

Deviation from the hammett relationship Hammett plot for aniline moiety: Hammett made a unique discovery²³ about the linear free energy relationships for the side chain. Application of the Hammett equation with the usual substituent constant σ to the $\log k_{\text{obs}}$ data of the *meta*- and *para*-substituted aromatic anils resulted in a non-linear concave downward curve (Fig. 3). Similar types of non-linear Hammett plots were observed previously in some reaction kinetics²⁴. The non-linear concave downward curve was obtained for the anils with substituents in aniline moiety. The electron-releasing substituents fall on the one side of the curve with a positive slope and the electron-withdrawing substituents on the other side with a negative slope. The isokinetic plot and Exner plot reveal that there is no change in reaction mechanism with respect to substituents in aniline moiety. *para*- and *meta*-Substituted anils with substituents in aniline moiety in aqueous acetic acid at 298-318 K confirm the Exner relationship, also the activation parameters to the isokinetic relationship but not to any of the linear free energy relationships.

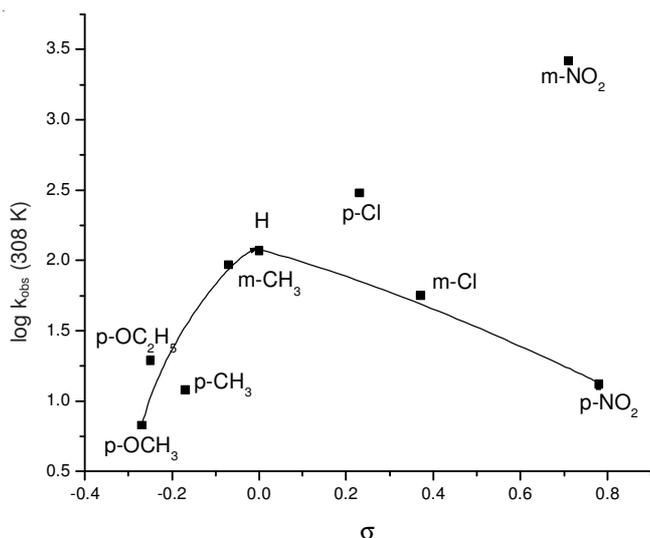


Fig. 3. Hammett plot for oxidation of aromatic anils by sodium perborate (substitution in aniline moiety) at 308 K

Isokinetic temperature is the temperature at which all the compounds react at same speed since this temperature variation of substituent has no influence on the free energy of activation.

In an isentropic oxidation, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series and the reactivity is determined by the entropy of activation²⁵.

$$\Delta H^\ddagger = \Delta H^\circ + \beta \Delta S^\ddagger$$

β is the isokinetic temperature and β was found to be 328 K which is greater than the experimental temperature.

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 isentropic oxidation reactions, only the enthalpy of activation finalizes the reactivity and if the isokinetic temperature is zero in isoenthalpic oxidation reactions, only the entropy of activation finalizes the reactivity²⁶. The values of the negative and positive ρ values, ρ^+ and ρ^- , respectively, at different temperature are given in Table-5. 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 INDC¹⁸. Ramalingam and Jayanthi¹⁸ have established the order dependence with respect to the reactants and other kinetic parameters of anils (substitution only in aniline moiety). The formation of oxalatochromate species is reported as the intermediate of the reaction since oxalic acid is used as catalyst.

TABLE-5 REACTION CONSTANT FOR THE SPB OXIDATION OF AROMATIC ANILS			
Substituents	Temperature (K)	ρ^+	ρ^-
Aniline moiety	298	4.14	0.34
	303	4.03	0.20
	308	4.32	0.02
	313	5.95	0.10
	318	4.42	0.01
Benzaldehyde moiety	298	1.52	2.06
	303	1.53	3.10
	308	2.04	3.80
	313	1.72	1.78
	318	1.14	0.18
Combination of aniline and benzaldehyde moiety	298	0.47	2.20
	303	0.81	2.44
	308	1.83	4.42
	313	0.71	2.96
	318	0.08	0.06

Hammett plot for benzaldehyde moiety: The non-linear concave upward curve was obtained for the anils with substituents in benzaldehyde moiety (Fig. 4). 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. The values of ρ^+ and ρ^- at five different temperatures are given in Table-5. The unsubstituted anil is also the less reactive in this series. But both the electron-releasing and withdrawing substituents

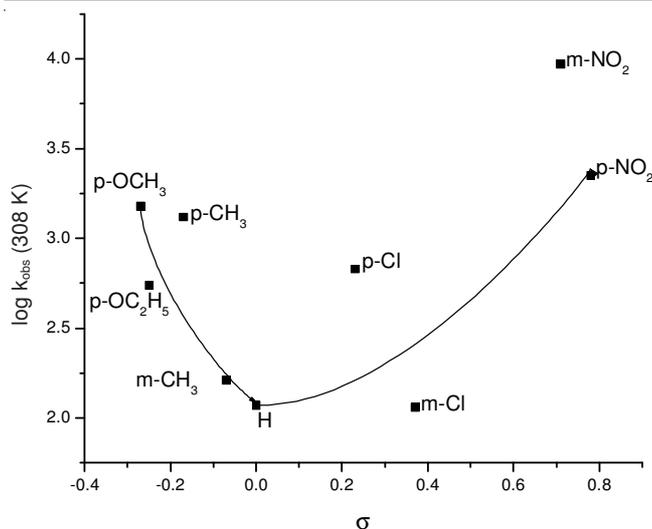


Fig. 4. Hammett plot for oxidation of aromatic anils by sodium perborate (substitution in benzaldehyde moiety) at 308 K

accelerate the rate of the reaction considerably dissimilar to aniline moiety. This shows the opposite kind of behaviour compared with aniline moiety.

Hammett plot for combination of aniline and benzaldehyde moiety: The non-linear concave upward curve was obtained for the anils with substituents in combination of aniline and benzaldehyde moiety (Fig. 5) and 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 like in substituents only in benzaldehyde moiety. The values of ρ^+ and ρ^- at five different temperatures are given in Table-5.

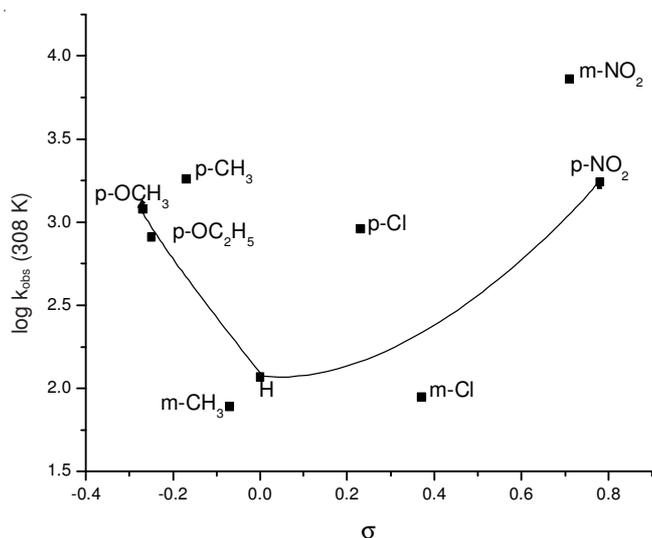


Fig. 5. Hammett plot for oxidation of aromatic anils by sodium perborate (substitution in combination of aniline and benzaldehyde moiety) at 308 K

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 state²⁷. The rate data obtained is also unsuccessful in proving that the typical Hammett equation $\log k_{\text{obs}}$ versus σ is a dispersed gram and a sensitive plot (Fig. 6) at the

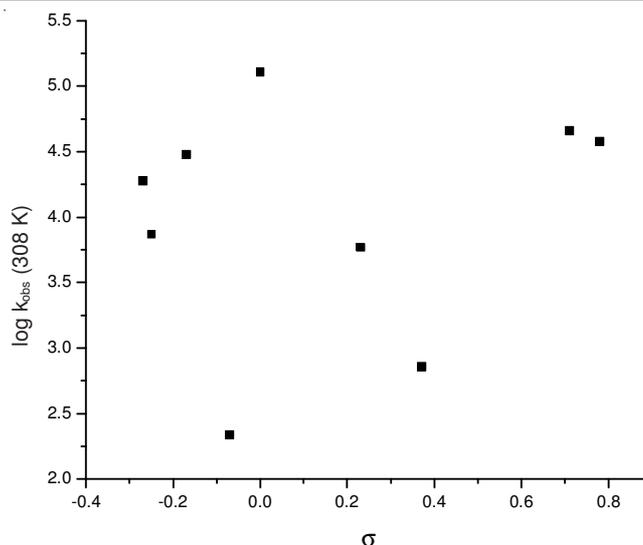


Fig. 6. Hammett plot for the oxidation of anils by sodium perborate

temperatures studied. The correlation coefficient (r) of the dispersed gram is found to be 0.155 with standard deviation of 0.947.

Literature study²⁸ 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 $p\text{-NO}_2$.

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 298, 303, 308, 313 and 318 K were analyzed 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.

The possible reason for the lack of free energy relationship is the isokinetic temperature 328 K which is greater than the experimental temperature. The same type of results was also reported by Elango and Buvanewari²⁹. Operation of inductive and resonance effect opposing each other is known but the present study has no parallel³⁰. 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 electrophile³¹. In some of the substituted anil exact compensation is doubtful and the resultant effect is experienced on the oxidation rate.

Conclusion

The reaction followed second order kinetics with respect to the concentration of [anil] and was the first order with respect to sodium perborate, respectively. Under the experimental conditions, 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. The correlations of oxidation rates substituted anils were correlated separately with any of the unit parameters which was also found to be ineffective. The oxidation rates analyzed in terms of dual substituent parameter equations was also found to be unsuccessful. Correlation of the experimental

data of solvent reveals that solvent interaction plays a major 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 sodium perborate. Non-linear concave downward curve of Hammett plot was obtained for the anils with substituents in the aniline moiety whereas the non-linear concave upward curve was obtained for the substituents in the benzaldehyde moiety and for the substituents in the combination of aniline and benzaldehyde moiety. With sodium perborate as oxygen donor, was proved to be a more effective oxidant in anils.

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