EFFECT OF SUBSTITUENTS ON COOXIDATION RATE OF AROMATIC ANILS AND OXALIC ACID BY CHROMIC ACID

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ABSTRACT

Though aromatic anils are said to be very sluggish towards Cr(VI) in presence of aqueous acetic acid medium, it can be easily oxidized in presence of oxalic acid, where it is proposed that an intermediate is formed between anil and a chromic acid –oxalic acid complex. The presence of the molecule of oxalic acid with in the complex facilitates the direct three electrons – reduction of Cr(VI) to Cr(III), which is the rate –limiting step, and the effect of various factors on rate of cooxidation were studied and reported earlier. The rate of oxidation was found to be a fractional order with respect anil and substituted anils, first order with respect to oxidant and fractional order with respect to oxalic acid. A number of substituted anils were prepared, purified and characterized and their effect on the cooxidation rate were studied at different five temperatures clearly shown that electron –releasing groups on both benzaldehyde and aniline moieties at the para position enhancing the rate of cooxidation whereas electron-withdrawing groups on both benzaldehyde and aniline moieties at para position retarding the rate of cooxidation. The thermodynamics parameters were computed and the isokinetic temperature computed from these plots is 502K.

KEYWORDS: Substituted Aromatic Anils; Cooxidation; Effect of substituents; Electron-releasing groups; Electron withdrawing groups.

INTRODUCTION

Benzylediene aniline or Schiff bases or Aromatic anils, X–CH=N–Y have two phenyl rings X and Y, the ring X-originates from the aromatic benzaldehyde moiety and Y from aniline moiety.
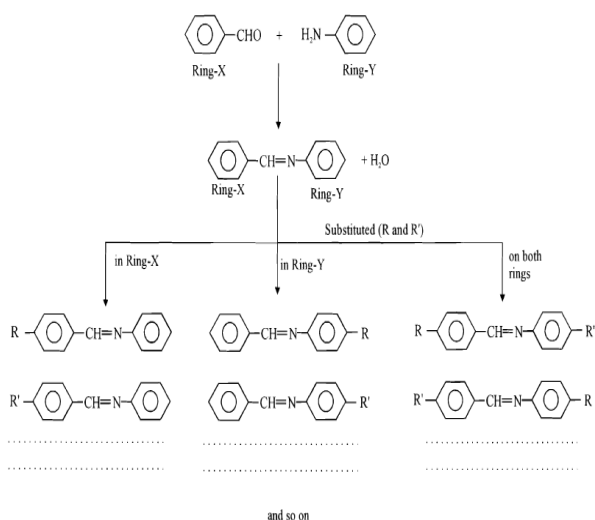
Literature scanning reveals that anils play differently towards different oxidizing agents. With lead tetra acetate in benzene medium, electron- releasing groups present in the anils enhance the rate of oxidation while the electron-withdrawing groups present in the anils retard the rate of oxidation.[1] Whereas in acetic acid medium the oxidation of anils is observed to be very fast, while with phenyl iodosoacetate in methylene chloride medium, it is smooth.[2] With acid bromate in H_2SO_4-HOAc mixture electron-releasing groups present in the anils retard the rate of oxidation while the electron-withdrawing groups , enhance the rate of oxidation.[3] With Mn(III) acetate in aqueous acetic acid medium electron-releasing groups present in the anils enhance the rate of oxidation, while electron-withdrawing groups retard the rate of oxidation.[4] With pyridinium chlorochromate in aqueous acetic acid, electron-releasing groups present in the anils retard the rate of oxidation, while the electron-withdrawing groups, enhance the rate of oxidation.[5] With N-chlorobenzamide in aqueous methanol medium, electron-releasing groups present in the anils enhance the rate of oxidation, whereas, the electron-withdrawing groups present in the anils retard the rate of oxidation.[6] But it observed that the oxidation

of anils with Cr(VI) in aqueous acetic acid medium is very sluggish.[7]

Literature survey indicate that chromic acid oxidation of a mixture of oxalic acid and isopropyl alcohol proceeds much faster than that of either of the two substrates. It is shown that both substrates undergo oxidation. It is also shown that the alcohol undergoes a two-electron oxidation and oxalic acid a one-electron oxidation. The intermediate is believed to formed from the alcohol and a chromic acid –oxalic acid complex.[8,9]

The unusually high reactivity of the complex composed of a molecule of chromic acid, oxalic acid and a molecule of the substrate suggests that a complex containing both components offers the reaction a more favorable pathway than the oxidation of a single molecule of a substrate, e.g., isopropyl alcohol leads to an unstable and very reactive chromium (IV) species. The presence of the molecule of oxalic acid within the complex facilitates the direct three-electron reduction of Cr (VI) to Cr (III), thus avoiding the formation of the energetically unfavorable Cr (IV), coupled with the formation of a very stable molecule of CO_2 and of a relatively stable free radical COOH- or COOH. It has been established that the undissociated form of oxalic acid is required for the formation of complex with Cr (VI).[10,11]

EXPERIMENTAL

Materials
Benzaldehyde and aniline were LR grade and were used after distillation as described in literature.[12] Substituted benzaldehydes, substituted anilines were AR grade. Aromatic Anils were prepared by the standard procedure,[13] recrystallized as described in the literature and their purities were checked by usual methods by comparing the melting points of anils with values given in the literature.[13] All other reagents used were Analar grade. Conductivity water was used throughout the course of the investigation. Acetic acid (AR) was twice distilled over chromic oxide containing acetic anhydride (bp 118˚C).

Kinetic Measurements
Solutions of substituted anils and chromic acid were prepared in aqueous acetic acid medium and oxalic acid prepared in water were thermally equilibrated for 2 h before each run. The reactions were carried out under pseudo –first order conditions by keeping an excess of [anils] and [Oxalic acid] over [oxidant], maintaining the ionic strength constant (0.2M) by adding sodium nitrate.

The kinetics of the reactions were studied in acetic acid medium 50% (v/v) in the blackened flasks to avoid any photochemical decomposition and the kinetics of the reactions were followed by monitoring the reduction of Cr(VI) by iodometry at different intervals of time. Under this condition of the experiments the solvent was not oxidized. Rate constant were computed from the linear

(r>0.99) plot of log [Oxidant] against time .in the evaluation of rate coefficients, the kinetics were followed to nearly 75% reaction. Duplicate kinetics run showed that the rates were reproducible with 3 %. The second order rate constant k_2 was obtained from the relation $k_2 = k_1/$ [anil] where k_1 is the pseudo-first order rate constant.

Product analysis
The product analysis was carried out under kinetic conditions .Under the specified conditions of cooxidation of aromatic anils and oxalic acid in aqueous acetic acid medium .it was observed that azobenzene is the only nitrogen containing major product of oxidation along with benzaldehyde .In the case of substituted anils containing substituents in the aniline moiety as well as in the aldehydes moiety, substituted azobenzenes are only nitrogen containing major product of oxidation along with substituted benzaldehydes. Since there is no evidence of the presence of benzoic acids, it can be confirmed that the further oxidation of benzaldehydes did not take place. Also, earlier studies lend a strong support for the products of oxidation.[14-18]

RESULTS AND DISCUSSION

The oxidation of substituted aromatic anils on aniline moiety and on both benzaldehye and aniline moieties by Cr (VI) in presence of oxalic acid in aqueous acetic acid medium showed the following features.

Order with respect to the oxidant
Under the condition [Substituted aromatic anils] >> [Cr (VI)], the order in [Cr (VI)] is unity as revealed by the linear plots of log [Cr (VI)] against time (Table-1, Figure-1).

Table 1: [Anil]   : 2 x 10^{-3} M Solvent: 50 % HOAc - 50% H_2O (v/v) [OxH$_2$]: 4 x 10^{-4} M Temp: 30 °C [Cr(VI)] : 4 x 10^{-4} M [NaCl]: 0.2M.

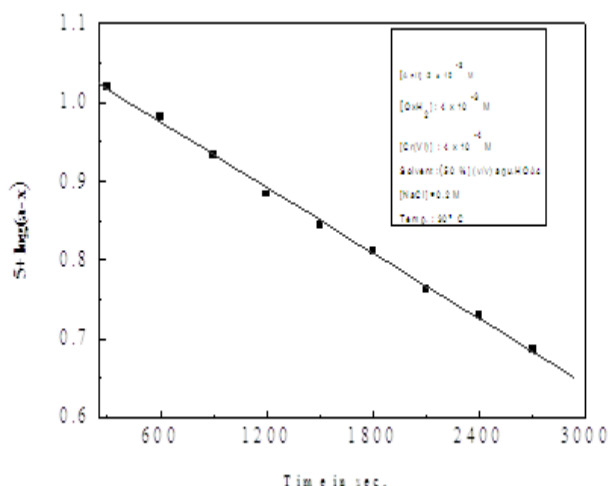| Time (in sec)	(a-x) x 10^3 M	k_1 x 10^4 S^{-1}
300	1.0463	
600	0.9583	
900	0.8565	
1200	0.7643	
1500	0.6991	3.104
1800	0.6459	
2100	0.5787	
2400	0.5362	
2700	0.4856	

Figure 1: First order plot.

The cooxidation reaction was also carried out by changing the concentrations of Cr (VI) from (2.0 x 10^{-4} M - 6.0 x 10^{-4} M) at constant concentration anil and at ionic strength 0.2 M in 50% (v/v) aqueous acetic acid medium (Table-2). Neither constant values of k_1 are observed nor an appreciable increase is noted in the rate constant values (k_1) with the increase of concentration of Cr (VI). But however, the ratio of the rate to concentration of Cr (VI)$_{tot}$ is constant and hence it can be inferred that the order with respect to the total [Cr(VI)] is one.[19]

Table 2: [Anil]: 2 x 10^{-3} M Solvent: 50 % HOAc -50% H$_2$O (v/v) [OxH$_2$]: 4 x 10^{-3} M Temp: 30 °c [NaCl]: 0.2M.

[Cr(VI)] : 4 x 10^4 M	k_1 x 10^4 s^{-1}	Rate : [Cr(VI)]$_{tot}$
1	0.87	0.87
2	1.62	0.81
3	2.39	0.79
4	3.22	0.81
5	3.83	0.77
6	4.41	0.74

Order with respect to aromatic anils

Follows fractional order in [unsubstituted aromatic anils] and [substituted aromatic anils] as revealed by the slopes of the plots of log k_1 against log [substrates] (Table-3, Figure-2).

Table 3: [OxH$_2$]: 4 x 10^{-3} M Solvent: 50 % HOAc - 50% H$_2$O (v/v) [Cr (VI)]: 4 x 10^{-4} M Temp: 30 °c [NaCl]: 0.2M.

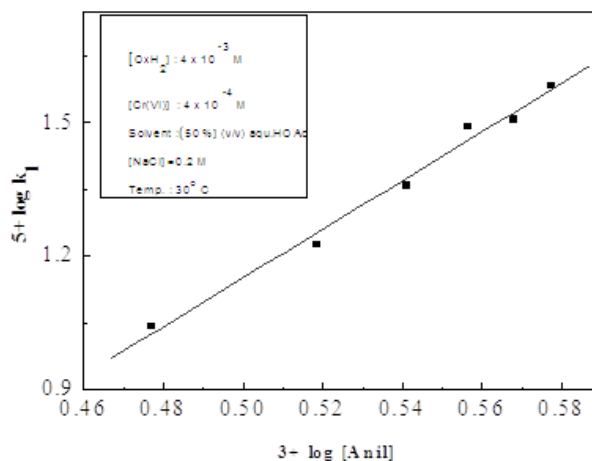| [Anil] x 10^3 M	k_1 x 10^4 s^{-1}
1	2.529
2	3.104
3	3.439
4	3.735
5	3.990
6	4.147

Figure 2: Variation of Anil.

Order with respect to oxalic acid, follows fractional order in oxalic acid as revealed by the slopes of the plots of log k_1 against log [oxalic acid] (Table-4, Figure-3).

Table 4: [Anil]: 2 x 10^{-3} M Solvent: 50 % HOAc -50% H$_2$O (v/v) [Cr (VI)]: 4 x 10^{-4} M Temp: 30 °c [NaCl]: 0.2M.

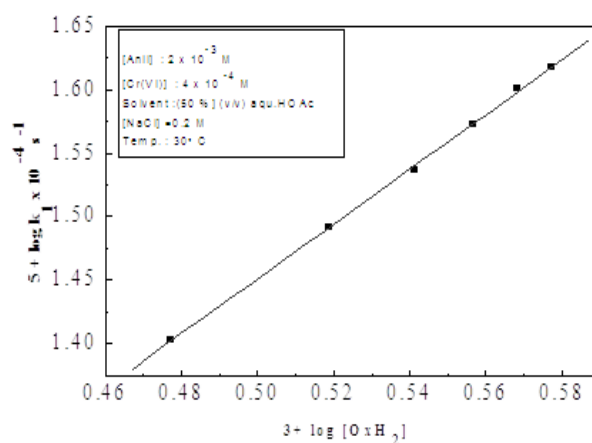| [OxH$_2$] x 10^3 M	k_1 x 10^4 s^{-1}
1	1.10
2	1.68
3	2.28
4	3.10
5	3.21
6	3.83

Figure 3: Variation of Oxalic acid.

Variation of aqueous acetic acid medium

A thought provoking results were obtained, when the cooxidation reactions were carried out at different concentrations of acetic acid, in acetic acid -water mixture. We witness that virtually there is no change in the rate of cooxidation. The rate of cooxidation of anils by Cr (VI) in presence of oxalic acid remain constant, though acetic acid proportion is increased in acetic acid - water mixture. Therefore, in all probability it can be rightly assumed that the following equilibrium exists

(Scheme-I) between anils and aqueous acetic acid as reported before.[20,21]
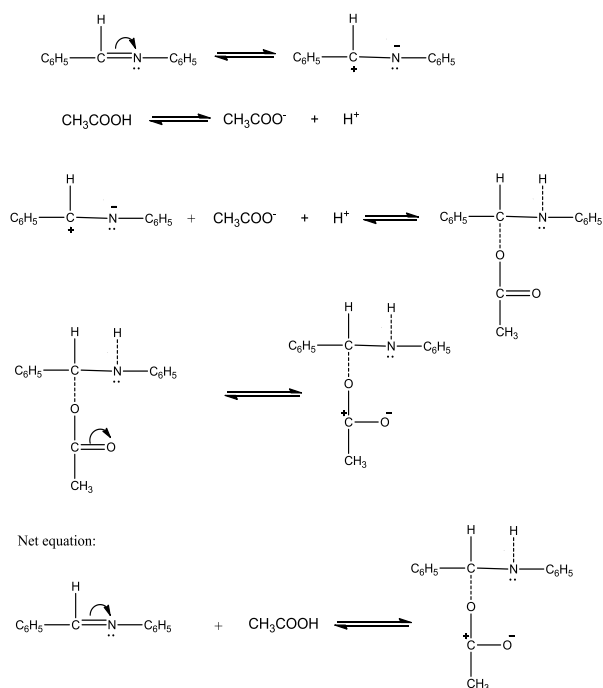
Scheme-I

When substituents are present in the benzaldehyde moiety of the aromatic anil

The substituents such as, methyl or methoxy groups present in the para position of the benzaldehyde moiety of the anil enhance the rate of cooxidation. And electron-withdrawing groups like chlorine atom, the nitro group at the para position of the benzaldehyde moiety of the anil brings down the rate of the cooxidation. Therefore among the electron-withdrawing groups like chlorine and nitro, it is the nitro group that plays an ideal role of bringing down the rate of cooxidation of aromatic anil, while electron -releasing groups enhance the rate of cooxidation. Summarizing the trend while different substituents are present in the benzaldehyde moiety of aromatic anil as reported before.[20,21]

p-CH$_3$O > p-CH$_3$ > Anil > p-CI > m-NO$_2$ > p-NO$_2$
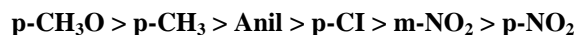
When substituents are present in the aniline moiety of the aromatic anil

1. Electron-releasing groups like methyl group enhances the rate of cooxidation of aromatic anil, even if it is present at the para position of aniline moiety of aromatic anil, and to our surprise we observe that the magnitude of enhancement is more or less same when methyl group is present at the benzaldehyde moiety of the anil or aniline moiety of the anil.

2. Among the chlorine substituted aromatic anils, surprisingly we witness that the magnitude, the retardation of the rate of cooxidation of benzylidene (p-Chloro) aniline from that of benzylidene aniline is much more than the magnitude in the retardation

of the rate of cooxidation p-Chloro benzylidene aniline from that of benzylidene aniline.

Anils   : Anil > pCI- > - Pci
K$_1$x10^{4}s^{-1} : 2.44   2.13   1.63

3. Nitro group play more havoc by bringing down the rate remarkably when compared to unsubstituted anil or nitro substituted anil at the benzaldehyde moiety of the anil or Chloro substituted anil.

4. Summarizing the trend while different substituents are present in the aniline moiety of aromatic anil.

Anils   : -p-CH$_3$ > Anil   > -p-CI > -p-NO$_2$
k$_1$x10^4 s^{-1} : 3.04   2.44   1.63   0.029
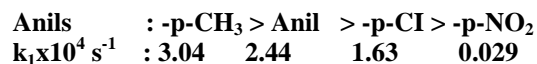
Summarizing the conclusions that we have arrived at by observing the rate of cooxidation of aromatic anil containing substituents either at the benzaldehyde moiety of the anil or at the aniline moiety of the anil

a) Irrespective of the moieties at which the substituents are present, that is whether they are present at the benzaldehyde moiety of the anil or at the aniline moiety of the anil, methyl and methoxy groups enhance the rate of cooxidation, and to our surprise the magnitude of enhancement is same, whether these groups are present at the benzaldehyde moiety of the anil or aniline moiety of the anil.

b) With regard to chlorine atom, chlorine atom retards the rate of cooxidation, than unsubstituted anil, but the magnitude of retardation is more if chlorine is present at the aniline part of the anil.

c) But the magnitude of retardation is very much pronounced in the case of nitro group at the aniline moiety of the anil.

Therefore, one can easily conclude that apart from electron –withdrawing tendency there is some other factor operating in Benzylidene (p-Nitro) aniline in bringing down the rate of cooxidation.

When the same or different substituents are present in both benzaldehyde and aniline moiety of the aromatic anil

a) When methyl groups are present at both the benzaldehyde and aniline moieties of anil, they enhance the rate of cooxidation than unsubstituted anil, and methyl substituted anil either at benzaldehyde moiety or aniline moiety of the anil.

b) Much retardation is not at all observed than Benzylidene aniline if we introduce nitro group at benzaldehyde moiety of the anil keeping methyl group at the aniline moiety of the anil.

c) Much retardation is observed when nitro group is introduced at the aniline moiety of the aromatic anil while whatever group is present at the benzaldehyde moiety of the aromatic anil.

d) We are wonder struck to observe that if nitro groups are present at both benzaldehyde moiety of the anil

and at aniline moiety of the anil, the retardation in cooxidation is even more.

e) Hence one can easily conclude that the rate enhancement or rate retardation may be due to the groups present at the aniline moiety of the anil and not due to groups present at benzaldehyde moiety of the anil.

Further it is more probable to conclude that nitro groups play more havoc, than chlorine, in bringing down the rate of cooxidation of anil, further it is observed that if nitro groups are present at both the benzaldehyde moiety of the anil as well as at the aniline moiety of the anil, the retardation is even more unimaginable.

DISCUSSION

The kinetic investigations so far studied can be compared with the results obtained by Rocek and Hasan,[22] Venkatasubramanian et al.[16] and Basheer Ahamed[23] except for the fact that the oxidation of anils is very sluggish in the absence of oxalic acid. It is observed that in the present investigation, the rate increases with the increasing concentration of oxalic acid. As suggested by Rocek and Hasan,[22] this behavior is characteristic of the formation of an intermediate complex. Therefore, it is worth to assume that chromic acid under the reaction conditions forms a complex with oxalic acid.[20,21]

Considering all the kinetic factors, scheme-II and III are proposed for the cooxidation of aromatic anils by Cr(VI) in presence of oxalic acid in aqueous acetic acid medium.
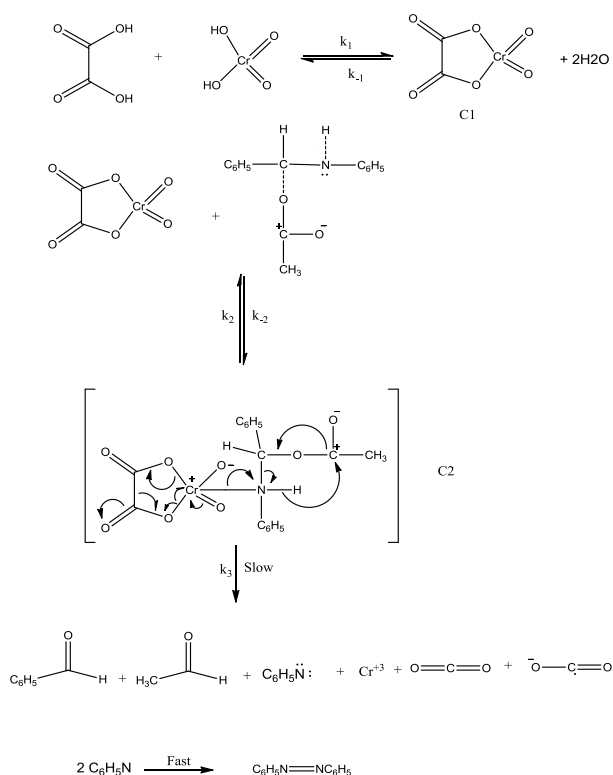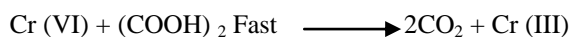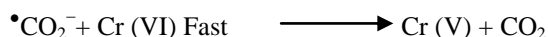
Scheme -II
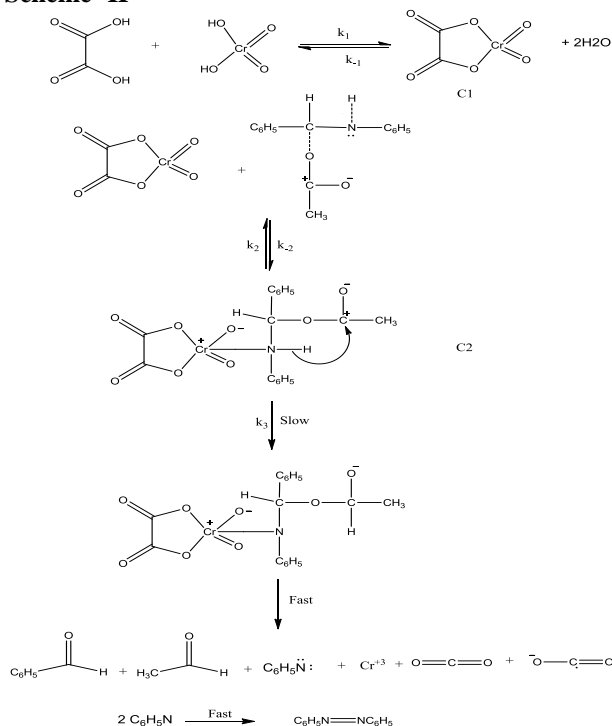
Scheme -III

According to scheme-II the Chromic acid -Oxalic acid complex (C$_1$) is coordinated to aromatic anils - acetic acid complex forming an activated complex (C$_2$) which then undergo concerted intramolecular electronic rearrangement to yield the products in one step.

According to scheme-III, the Chromic acid -oxalic acid complex (C$_1$) is coordinated to aromatic anils - acetic acid complex forming a coordinated complex (C$_2$), in which a hydride shift takes place in a slow step forming a highly unstable entity which then decomposes in a fast step to give the products.

Addition of aluminium nitrate suppresses the oxidation of aromatic anils with Cr (VI) in the presence of oxalic acid. Chatterjee and coworkers[24] have reported that the chromic acid oxidation of oxalic acid can be effectively prevented by the addition of aluminum nitrate. This effect is probably due to the ability to complex rather firmly with oxalic acid, and thus the formation of the oxalic acid-chromic acid complex, which is an intermediate in the oxidation reaction, is hindered. Rocek and Hasan[22] also report that the rate-accelerating effect of oxalic acid is almost canceled by the addition of aluminum nitrate. These results are in good agreement with the conclusion that the chromic acid-oxalic acid complex is an intermediate in the cooxidation reaction. The unusual high reactivity of the complex composed of a molecule of chromic acid and oxalic acid and a molecule of substrate is explained in this way[22] that a complex containing both components offers the reaction a more favourable pathway than the oxidation of a single molecule. The presence of the molecule of oxalic acid within the complex facilitates the reduction of Cr(VI)

directly to Cr(III), a direct three-electron reduction coupled with the formation of a very stable molecule of carbon dioxide and $^\bullet COOH$ species, thus avoiding the formation of the energetically unfavourable Cr(IV).[22] The fate of $^\bullet CO_2^-$ is explained as.

$$^\bullet CO_2^- + Cr\ (VI)\ Fast \longrightarrow Cr\ (V) + CO_2$$

$$Cr\ (VI) + (COOH)_2\ Fast \longrightarrow 2CO_2 + Cr\ (III)$$

Earlier studies lend strong support for this scheme (25). The activation enthalpies and entropies of the oxidation of anils by Cr(VI) in the presence of oxalic acid in aqueous acetic acid medium are linearly related (Table-5, Figure 4).

Table 5: Effect of Temperature and Activation parameters of oxidation of substituted aromatic anils.

[Anil]: 2×10^{-3} M;   [OxH$_2$]: 4×10^{-3} M
[Cr(VI)]: 4×10^{-4} M ;   Solvent: 50 % HOAc -50% H$_2$O (v/v) [NaCl]: 0.2M

| S. No.	[Anil] X–CH=N–Y	k2 x 10 lit mol-1 s-1					ΔH# kJ mol-1	-ΔS# J K-1 mol-1	ΔG# kJ mol-1	Ea kJ mol-1 K-1	R
		303 °K	308 °K	313 °K	318 °K	323 °K					
1.	H	1.22	1.60	2.25	3.03	4.10	47.60	99.05	80.12	50.11	0.98
2.	p-CH3-	1.55	1.95	2.64	3.62	4.17	44.09	116.9	79.51	46.60	0.98
3.	p-CH3O-	1.61	2.06	2.68	3.76	4.56	40.05	129.9	79.41	42.56	0.98
4.	p-Cl-	1.07	1.53	2.13	2.68	3.98	50.89	97.56	80.46	53.40	0.98
5.	m-NO2-	1.03	1.43	1.98	2.71	3.67	49.69	101.9	80.56	52.20	0.98
6.	p-NO2-	0.95	1.30	1.81	2.51	3.86	53.97	88.41	80.75	55.38	0.98
7.	-p-CH3	1.52	2.08	2.80	3.74	4.95	45.75	111.9	79.56	48.26	0.98
8.	-p-Cl	0.82	1.20	1.75	2.51	3.28	55.22	85.54	81.14	57.74	0.98
9.	-p-NO2	1.48	2.17	3.15	4.50	6.37	57.26	112.3	91.31	59.76	0.98
10.	p-CH3O-p-Cl	0.73	1.08	1.56	2.28	3.28	59.01	73.99	81.42	61.52	0.99
11.	p-CH3-p-NO2	0.038	0.057	0.078	0.11	0.15	58.65	99.82	88.89	61.16	0.98
12.	m-NO2-p-Cl	0.58	0.87	1.26	1.90	2.75	61.38	68.12	82.01	63.89	0.98
13.	p-CH3-p-CH3	1.88	2.27	2.78	3.37	4.16	29.98	161.8	79.02	32.49	0.98
14.	p-CH3O-p-CH3	1.78	2.36	3.09	3.99	5.13	40.71	126.8	79.16	43.22	0.99
15.	p-NO2-p-CH3	1.09	1.41	1.99	2.81	3.74	50.56	98.58	80.18	53.05	0.99
16.	p-CH3-p-NO2	0.038	0.052	0.075	0.103	0.140	52.72	122.9	88.95	52.28	0.99
17.	p-NO2-p-NO2	0.022	0.034	0.053	0.071	0.11	62.78	190.8	90.30	65.24	0.98
18.	p-Cl-p-CH3	0.96	1.36	1.83	2.55	3.56	50.84	98.69	80.74	53.35	0.98
19.	p-CH3-p-Cl	0.98	1.39	1.92	2.64	3.77	52.34	93.60	80.68	54.84	0.99
20.	p-Cl-p-Cl	0.79	1.11	1.52	2.19	3.12	53.65	90.99	81.22	56.16	0.98
21.	p-Cl-p-Br	0.83	1.21	1.68	2.28	3.45	54.28	88.55	81.11	56.78	0.98
22.	p-NO2-p-Cl	0.069	0.095	0.126	0.182	0.264	52.01	97.45	81.54	54.52	0.98
23.	p-Cl-p-NO2	0.033	0.048	0.066	0.096	0.134	55.23	112.41	89.29	57.74	0.98
24.	p-Cl-m-NO2	0.036	0.052	0.076	0.107	0.151	56.25	108.26	80.05	58.76	0.99
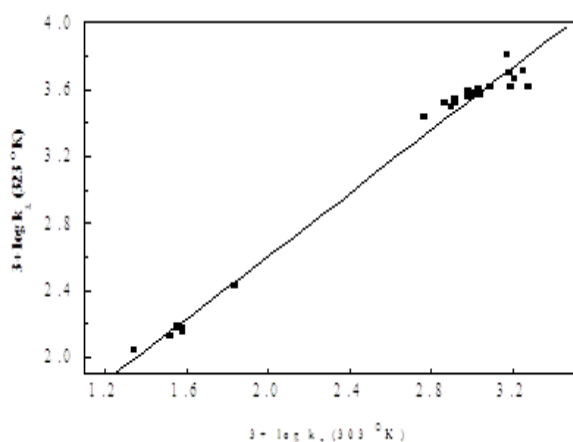
Figure 4: Exner's plot.

The correlation is tested and found genuine by applying Exner's Criterion (26). The isokinetic temperature computed from these plots is 502 K (Figures 5, 6).
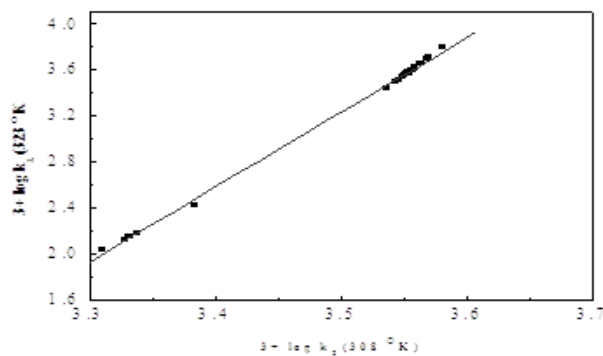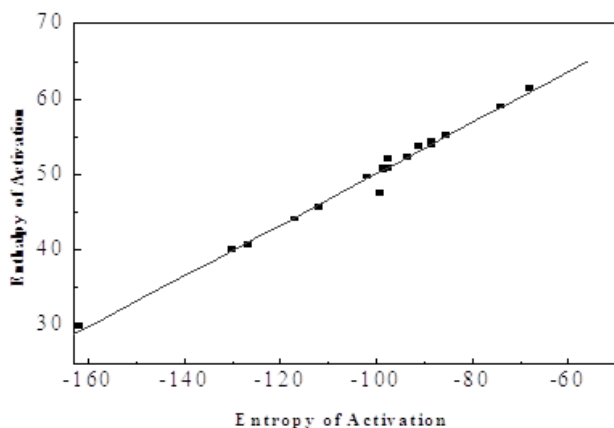

Figure 5: Exner's plot.

Figure 6: $\Delta H^{\#}$ vs. $\Delta S^{\#}$

ACKNOWLEDGEMENT

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