

Cooxidation of Aromatic Anils and Oxalic Acid by Chromic Acid in Aqueous Acetic Acid Medium

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The kinetic study of the oxidation of aromatic anil and its five derivatives in presence of oxalic acid by chromic acid in aqueous acetic acid medium has been studied. The reaction involves three electron transfer due to conversion of Cr(VI) to Cr(III). The cooxidation reveals the first order kinetics for the oxidant Cr(VI), fractional orders (0.50) and (0.76) for substrate and oxalic acid, respectively. A suitable mechanism and activation parameters have been computed.

Key Words: Aromatic anils, Oxalic acid, Cooxidation, Chromic acid.

INTRODUCTION

Aromatic anils have two phenyl rings, one derived from benzaldehyde and another from aniline. We can have substituents in either of two phenyl rings and oxidation study of the compounds have been carried out by chromic acid in presence of oxalic acid. The process is said to be co-oxidation. The oxidation was found to be sluggish in the absence of oxalic acid. But in presence of oxalic acid, the reaction was very effective.

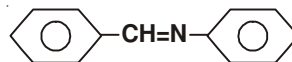
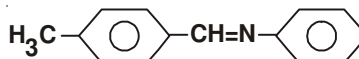
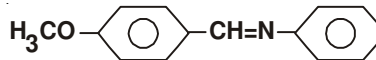
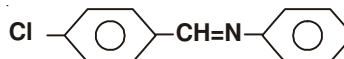
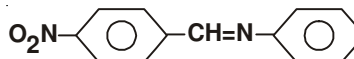
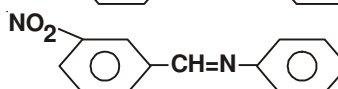
Chromium trioxide dissolves in water accompanying depolymerization¹ and the resulting solution is a fairly strong acid². In aqueous solution it gives mainly as HCrO_4^- which acts as the strong oxidizing species. The conversion of Cr(VI) to the stable Cr(III) during the reaction involves three electron transfer. The oxidizing power of Cr(VI) is influenced by the substituents in the substrate and the nature of the reaction medium. Oxidation of olefins^{3,4}, alcohols⁵⁻¹⁵, malachite green¹⁶ by Cr(VI) have been studied. The cooxidation of piperidin 4-ol¹⁷ and anilides¹⁸ have also been carried out by chromic acid in presence of oxalic acid. The present study devoted to the kinetics of cooxidation of aromatic anils with chromium(VI) in presence of oxalic acid in aqueous acetic acid medium.

EXPERIMENTAL

The benzylideneaniline (BA) and the substituted anils in the ring (B) given below were prepared by standard methods^{19,20}.

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Benzylidene aniline (BA)

*p*-Methylbenzylidene aniline*p*-Methoxybenzylidene aniline*p*-Chlorobenzylidene aniline*p*-Nitrobenzylidene aniline*m*-Nitrobenzylidene aniline

The purity of the compounds was checked by IR and TLC studies and comparing the physical constants. All the kinetic measurements were carried out in double distilled water and followed by iodometric titrations. The pseudo first order rate constants were calculated and the activation energies were obtained graphically by plotting $\log k_2$ versus $1/T$

Product analysis: Anil (0.1) M, oxalic acid (0.1) M, CrO_3 (0.01) M were taken in 50 % aqueous acetic acid medium in well cleaned stoppered bottle. The reaction was allowed for 12 h at 40 °C for completion. The products were extracted using ether, separated confirmed by TLC and chemical analysis. The compounds were identified azobenzene and benzaldehyde.

RESULTS AND DISCUSSION

The oxidation of anils by Cr(VI) in presence of oxalic acid in aqueous acetic acid medium at constant ionic strength was carried out. The oxidation reaction showed the following features:

(i) The oxidation of benzylidene aniline (BA) showed first order with respect to Cr(VI) under the condition of $[\text{anil}] \gg [\text{Cr(VI)}]$ revealed by the linear plot of $\log(a-x)$ versus time (Table-1).

TABLE-1
 $[\text{BA}] = 2 \times 10^{-3}$ M; Solvent = 50 % HOAc/ H_2O (v/v); $[\text{OxH}_2] = 4 \times 10^{-3}$ M
 $[\text{NaCl}] = 0.2$ M $[\text{Cr(VI)}] = 4 \times 10^{-4}$ M, Temp. = 30 °C

Time (s)	$(a-x) \times 10^3$ M	$k_1 \times 10^4 \text{ S}^{-1}$
300	1.296	
600	1.180	
900	1.083	
1200	0.967	
1800	0.791	2.4438
2400	0.726	
3000	0.652	
3600	0.578	

(ii) The order of reaction at different concentration of BA at constant ionic strength follows fractional order with respect to substrate (Table-2).

(iii) The order of cooxidation reaction with respect to oxalic acid from (1.0×10^{-3} to 6.0×10^{-3} M) at constant [BA] and Cr(VI) showed the fractional order (0.76) (Table-3).

TABLE-2

Solvent: 50 % HOAc/H₂O (v/v);
[OxH₂] = 4×10^{-3} M; [NaCl] = 0.2 M;
[Cr(VI)] = 4×10^{-4} ; Temp. = 30 °C

[BA] × 10 ⁻³ M	k ₁ × 10 ⁴ s ⁻¹
1	1.788
2	2.443
3	3.024
4	3.522
5	3.928
6	4.314

TABLE-3

[BA] = 2×10^{-3} M; Solvent: 50 %
HOAc/H₂O (v/v); [Cr(VI)] = 4×10^{-4} M;
Temp. = 30 °C; [NaCl] = 0.2 M

[OxH ₂] × 10 ⁻³ M	k ₁ × 10 ⁴ s ⁻¹
1	0.876
2	1.343
3	1.828
4	2.443
5	3.003
6	3.329

(iv) The various changes of percentage of AcOH medium under constant concentration of all the reagents, revealed no appreciable change in the rates of oxidation (Table-4).

TABLE-4

[BA] = 2×10^{-3} M; [NaCl] = 0.2 M; [OxH₂] = 4×10^{-3} M;
Temp. = 30 °C; [Cr(VI)] = 4×10^{-4} M

Solvent composition		k ₁ × 10 ⁴ s ⁻¹
HOAc	H ₂ O (v/v)	
25	75	2.014
30	70	2.234
35	65	2.342
40	60	2.371
45	55	2.404

(v) The kinetic study on the effect of changing ionic strength of the medium (0 - 2.0×10^{-2} M) during the cooxidation at constant condition of the other reagents showed, no considerable changes in the rates (Table-5).

TABLE-5

[BA] = 2×10^{-3} M; Solvent = 50 % HOAc/H₂O (v/v);
[OxH₂] = 4×10^{-3} M; Temp. = 30 °C; [Cr(VI)] = 4×10^{-4} M

[NaCl] × 10 ⁻² M	k ₁ × 10 ⁴ s ⁻¹
0	2.68
1	2.68
4	2.66
8	2.64
12	2.62
16	2.51
20	2.44

(vi) The rates of reactions increased linearly with increase in (H⁺) ions either by adding dilute sulphuric acid (0.2 M) or dilute perchloric acid (0.35 M) (Table-6).

TABLE-6
[BA] = 2 × 10⁻³ M; Solvent = 50% HOAc/H₂O (v/v); [OxH₂] = 4 × 10⁻³ M;
[NaCl] = 0.2 M; [Cr(VI)] = 4 × 10⁻⁴ M; Temp. = 30 °C

[H ⁺] ^{×10⁻³} M	HClO ₄ k ₁ × 10 ⁴ s ⁻¹	H ₂ SO ₄ k ₁ × 10 ⁴ s ⁻¹
2	4.67	6.98
8	7.46	9.20
20	9.77	10.99
50	14.75	13.24

(vii) Addition of pyridine suppressed the cooxidation reaction which did not reveal as a base catalyzed reaction. The suppression in the rate may be due to intermediate complex formation between (oxalic acid-chromic acid complex) and pyridine (Table-7).

(viii) The activation parameters of the cooxidation of BA were calculated at the reaction temperature between 303 and 323 K (Table-8).

TABLE-7
[BA] = 2 × 10⁻³ M; Solvent = 50 %
HOAc/H₂O (v/v); [OxH₂] = 4 × 10⁻³ M;
[NaCl] = 0.2 M; [Cr(VI)] = 4 × 10⁻⁴ M;
Temp. = 30 °C

[Added pyridine] × 10 ⁻² M	k ₁ × 10 ⁴ s ⁻¹
0	2.443
2	1.449
4	0.891
12	0.284
16	0.123

TABLE-8
[BA] = 2 × 10⁻³ M; Solvent = 50 %
HOAc/H₂O (v/v); [OxH₂] = 4 × 10⁻³ M;
[NaCl] = 0.2 M; [Cr(VI)] = 4 × 10⁻⁴ M

Temperature (K)	k ₂ × 10 L mol ⁻¹ s ⁻¹
303	1.22
308	1.60
313	2.25
318	3.02
323	4.10

TABLE-9
ACTIVATION PARAMETER

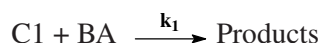
Anils	Rate constants k ₁ × 10 ⁴ s ⁻¹	E _a (KJ mol ⁻¹)	ΔS [‡] (Jdeg ⁻¹ mol ⁻¹)	ΔH [‡] (KJ mol ⁻¹)	ΔG [‡] (KJ mol ⁻¹)
BA	2.44	50.106	-99.045	47.597	80.119
<i>p</i> -CH ₃ BA	3.10	46.597	-116.913	44.087	79.511
<i>p</i> -OCH ₃ BA	3.22	42.555	-129.934	40.045	79.415
<i>p</i> -Cl BA	2.13	53.400	-97.563	50.891	80.456
<i>p</i> -NO ₂ BA	1.90	55.376	-88.408	53.965	80.751
<i>m</i> -NO ₂ BA	2.05	52.204	-101.909	49.693	80.555

From the above results, it is noted that the electron releasing group increases the rate of the reaction when compared to unsubstituted anil.

When the substituents are present in the benzaldehyde moiety of aromatic anil, the following findings were recognized. (i) The electron releasing group like methyl (or) methoxy present in the *p*-position of benzaldehyde moiety of the anil enhance the rate of cooxidation. (ii) The chlorine present in *p*-position doesnot bring down the cooxidation rate appreciably. (iii) The nitro group at the *p*-position brings down the rate of cooxidation appreciably.

Based on the present results the rate increases with increasing concentration of oxalic acid. This behaviour is characteristic of the formation of an intermediate complex. Therefore it is assumed that the chromic acid under the reaction conditions forms a complex with oxalic acid.

The fractional order of the oxidation with respect to substrate BA (0.50), first order with respect to oxidant Cr(VI) and fractional order (0.76) with respect to oxalic acid have been proved by assuming the following mechanism.



where C_1 is 1:1 complex of oxalic acid and chromic acid.

$$\text{Therefore; } C_1 = \frac{K_1[\text{COOH}]_2[\text{Cr(VI)}]_{\text{tot}}}{1 + K_1[\text{COOH}]_2}$$

where $[\text{Cr(VI)}]_{\text{tot}} = [\text{Cr(VI)}] + [C_1]$; $[\text{BA}]/k_{\text{Exp}} = (1/k) + (1/k) K_1 [(\text{COOH})_2]$.

The oxidation of ternary system may correctly be assumed to consist of two independent reactions occurring simultaneously, since the oxidation of anils with Cr(VI) was very sluggish in the absence of oxalic acid.

Therefore, the following rate law is proposed.

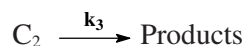
$$\frac{-d[\text{Cr(VI)}]}{dt} = k_1 [\text{BA}]^{0.50} [\text{OxH}_2]^{0.76} [\text{Cr(VI)}] + k_2 [\text{OxH}_2]^2 [\text{Cr(VI)}]$$

$$= k_{\text{obs}} [\text{Cr(VI)}]$$

$$k_{\text{obs}} = k_1 [\text{BA}]^{0.50} [\text{OxH}_2]^{0.76} + k_2 [\text{OxH}_2]^2$$

$$\therefore k_{\text{obs}} = k_1 [\text{BA}]^{0.50} [\text{OxH}_2]^{0.76}$$

$$\frac{k_{\text{obs}}}{[\text{BA}]^{0.50}} = k_1 [\text{OxH}_2]^{0.76}$$



$$\text{Rate} = k_3 [C_2] = k_{\text{obs}} [\text{Cr(VI)}]$$

$$[\text{Cr(VI)}]_{\text{tot}} = [\text{H}_2\text{CrO}_4] + K_1[\text{OxH}_2] [\text{H}_2\text{CrO}_4] + K_2 K_1 [\text{OxH}_2] [\text{H}_2\text{CrO}_4] [\text{BA}]$$

Rearranging we get,

$$k_3 [C_2] = k_{\text{obs}} [\text{H}_2\text{CrO}_4] \{ 1 + K_1[\text{OxH}_2] + K_2 K_1 [\text{OxH}_2] [\text{BA}] \}$$

$$= k_3 K_2 K_1 [\text{OxH}_2] [\text{H}_2\text{CrO}_4] [\text{BA}]$$

$$\frac{[\text{OxH}_2]}{k_{\text{obs}}} = \left(\frac{1}{k_3 K_2 K_1} + \frac{[\text{OxH}_2]}{K_2 K_1} \right) \left(\frac{1}{[\text{BA}]} + \frac{[\text{OxH}_2]}{k_3} \right)$$

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