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Substituents effect on cooxidation rate of chalcones and oxalic acid using chromium (VI)

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ABSTRACT

Chalcones (CHAL)were synthesized from substituted benzaldehyde and acetophenone, benzaldehyde and substituted acetophenone and substituted benzaldehyde and substituted acetophenone subjected to the cooxidation in presence ***of*** *oxalic acid in aqueous acetic acid medium by chromic acid (Cr (VI)). The reactions were carried out under pseudo–first order condition, and the rate of cooxidation was found to be a unity order with respect to the [Cr (VI)], a fractional order with respect to substituted chalcones and the order with respect to oxalic acid is a fractional order. The effect of various parameter such as [H^+], [NaCl],[NaO_3],[pyridine]on rate of cooxidation were studied, the dielectric constant of the medium have no effect on reaction rate. Comparative study of the rates of cooxidation of substituted chalcones, were done and shown the presence of electron-releasing group at para position increases the rate of cooxidation and electron-withdrawing group at para position retards the rate of cooxidation.*

Keywords: substituted chalcones; chalcones; cooxidation; chromic acid; oxalic acid.

INTRODUCTION

The oxidizing power of chromic acid well known and its ability to oxidize almost all organic compounds and some inorganic compound, Chromic acid [Cr(VI)] is an important and useful tool in the hands of chemists both for preparative and analytical purposes over a century. Many studies of the kinetics and mechanism were carried out using chromic acid as an oxidizing agents[1-5].

Many features in the kinetics and mechanistic study of the oxidation of many alcohols by [Cr(VI)],the chromic acid oxidation of a mixture of oxalic acid and isopropyl alcohol proceeds much faster than the oxidation of either of the two substrates alone have been reported by many workers, they observed a very remarkable observation that the alcohols undergo, a two – electron oxidation and oxalic acid a one - electron oxidation [6-10] and some other studies have been used [Cr(VI)] as an oxidant [11-17].

The importance of chalcones or phenyl styryl ketones because they have a unique structural feature of having a C=O functional group in conjugation with C=C and the whole molecule is in conjugation. It exhibits various biological activities and also its utility in synthesis of various heterocyclic compounds. They have been reported as plant origin, antioxidant, antimalarial, antiflammatory, antitumour, antifibrogenic, anticancer, antitrichomonal, antileishmanial, cytotoxic and anti-Trypanosoma cruzi and antibacterial activities [18-26]. The presence of a reactive α-β-unsaturated keto function in chalcones is found to be responsible for their antimicrobial activity that may be altered depending on the type and position of substituent on the aromatic rings.

The literature scanning shows that the kinetics and mechanism of oxidation involving chalcones or phenyl styryl ketones were carried out using different oxidants, In our previous work Yousif et al. [27], we have shown the features of kinetics and mechanism of cooxidation of chalcones and oxalic acid by chromic acid in aqueous acetic acid medium and based on the kinetics data we have proposed a suitable mechanism for the reaction, different oxidizing agents have reported for the oxidation of chalcones and in all these reactions either >C=C<or >C=O< is attacked by various oxidants that have been used for the oxidation of chalcones as reported [28-48]our interest to continue the study of cooxidation of substituted chalcones and oxalic acid in aqueous acetic acid medium and to compare the rates and the effect of substituents on the cooxidation reactions.

EXPERIMENTAL SECTION

All chemicals were AR grade, benzaldehyde and acetophenone were used after distillation as described in literature [49].Substituted benzaldehydes, substituted acetophenone were AR grade and were used as such. Chalcones were prepared by the standard procedure [47], recrystallized as described in the literature and their purities were checked by usual methods by comparing the melting points of chalcones with values given in the literature[50]. Conductivity water was used throughout the course of the investigation. Acetic acid (AR) was twice distilled over chromic oxide containing acetic anhydride[51] (bp. 118˚C).

Solutions of chalcones and chromic acid were prepared in acetic acid, oxalic acid prepared in water; all solutions were thermally equilibrated for 2 h before each run. The reactions were carried out under pseudo –first order conditions by keeping an excess of [chalcones] 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) iodometrically at regular intervals of time. Under this conditions of the experiments the solvent were 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 $k_2 = k_1$/[Substituted chalcones] where k_1 is the pseudo-first order rate constant.

The product analysis was carried out under kinetic conditions .Under the specified conditions of cooxidation of substituted chalcones and oxalic acid in aqueous acetic acid medium .It was observed that substituted benzoic acid and substituted phenyl acetaldehyde were detected by TLC and IR spectrum and they compared with those of authentic samples . The liberation of CO_2 during the oxidation was detected as described earlier [27].

RESULTS AND DISCUSSION

In our previous study of the cooxidation of chalcones and oxalic acid by Cr (VI) in aqueous acetic acid medium was carried out at 308K showed the following features, which have reported earlier Yousif etal. [27].

Effect of varying the [Oxidant]

The order with respect to the [Cr (VI)] under the condition [substituted chalcones]>> [Cr (VI)], the order in [Cr (VI)] is unity as revealed by the linear plots of log [Cr (VI)] against time.

Effect of varying [Chalcones]

The order with respect to chalcones follows fractional order and a fractional order for the [substituted chalcones] as revealed by the slopes of the plots of log $k_1$against log [substrates]. (Table 1.Figure 1 a).

Table- 1: Effects of varying [reactants] on the reaction rate (Yousif Algamal et al. [27])
I = 0.2 mol dm^{-3};Temp: 308 K; Solvent: HOAc (50% v/v)

10^3 [CHAL] Mol dm^{-3}	**10^4 [Cr(VI)] Mol dm^{-3}**	**10^3 [OxH_2] Mol dm^{-3}**	**10^4 k_1 (S^{-1})**					
			CHAL	**CH_3O- CHAL**	**CH_3- CHAL**	**Cl- CHAL**	**Br- CHAL**	**NO_2-CHAL**
2	4	4	0.08245	0.1905	0.1234	0.05435	0.04658	0.000218
4	4	4	0.2047	0.3548	0.2435	0.13847	0.07445	0.000456
6	4	4	0.39012	0.6012	0.6312	0.23345	0.10495	0.000723
8	4	4	0.61153	0.9675	0.9403	0.3668	0.12346	0.002345
10	4	4	1.05224	1.4624	1.6242	0.61372	0.16042	0.005623
		r slope	0.99 2.05	0.98 1.90	0.98 1.89	0.98 2.05	0.99 --	0.99 --
2	2	4	0.0428	0.1234	0.1134	0.03435	0.03581	0.000123
2	4	4	0.08245	0.2436	0.1424	0.06724	0.09445	0.000218
2	6	4	0.1845	0.4321	0.2144	0.12824	0.10245	0.002454
2	8	4	0.2436	0.7824	0.3211	0.2458	0.16824	0.006827
2	10	4	0.3210	1.2346	0.4234	1.2020	0.19846	0.012345
2	4	2	0.08245	1.2338	0.0934	0.05218	0.04215	0.000891
2	4	4	0.20125	1.6234	0.3503	0.10445	0.06248	0.000218
2	4	6	0.43216	1.9056	0.7322	0.16289	0.08286	0.006024
2	4	8	0.71886	2.0124	1.1981	0.21889	0.09953	0.01545
2	4	10	1.04956	2.4568	1.6982	0.26117	0.11998	0.02456
		r slope	0.98 1.60	0.98 1.65	0.99 1.60	0.99 1.60	0.99 --	0.97 --

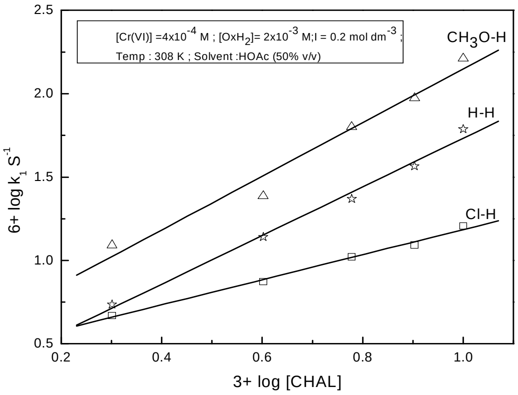

Fig.1a: Variation of Chalcones

Effect of varying [Oxalic acid]

The 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 1., Figure 1b).

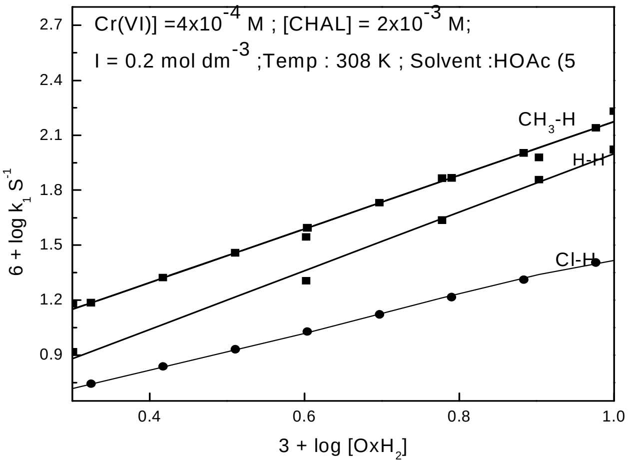

Fig.1b: Variation of Oxalic acid

Effect of Acetic acid

We witness that virtually there is no change in the rate of cooxidation. The rate of cooxidation of chalcones by Cr (VI) in presence of oxalic acid remain constant, though acetic acid proportion is increased in acetic acid -water mixture (Table2). Therefore, in all probability it can be rightly assumed that an equilibrium exists between chalcones and aqueous acetic acid[27].

Table -2: Effects of Solvent HOAc –H_2O on the reaction rate: (YousifAlgamal et al. [27])
[CHAL] = 2.0 x 10^{-3}moldm^{-3} ; [Cr(VI)] = 4.0 x10^{-4} mol dm^{-3}
[OxH_2] = 4.0 x 10^{-3}mol dm^{-3} ; I = 0.2 mol dm^{-3}; Temp: 308 K ;

Solvent : HOAc-H_2O (% v/v)	10^4k_1(S^{-1})
20	0.081412
30	0.07821
40	0.08012
50	0.082452
60	0.07602
70	0.08134

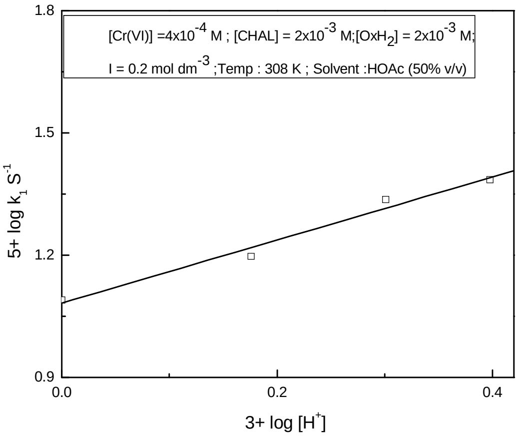

Fig.2: Variation of [H^+]

Effect of $[H^+]$

The rate of cooxidation increases with an increase of $[H^+]$ and the log-log plot of initial rate against $[H^+]$ gave a straight line with slope = 0.75 indicating the order with respect to $[H^+]$ is a fractional [Figure 2].

Effect of $[NaNO_3]$

The rate of oxidation of chalcones remain constant when the ionic strength of the medium is increased.Effect of adding sodium chloride also studied and there is no change in the rates of oxidation of chalcones by the addition of sodium chloride .And addition of aluminum nitrate suppresses the oxidation of chalcones with Cr(VI) in presence of oxalic acid .(Table 3).

Table -3: Effects of adding Aluminum nitrate on the reaction rate: (YousifAlgamal et al. [27])
$[CHAL] = 2.0 \times 10^{-3}$ moldm^{-3} ; $[Cr(VI)] = 4.0 \times 10^{-4}$ mol dm^{-3}
$[OxH_2] = 4.0 \times 10^{-3}$ mol dm^{-3}; I = 0.2 mol dm^{-3}; Temp: 308 K; Solvent: HOAc (50% v/v)

[Aluminum nitrate]M	$10^4 k_1 (S^{-1})$
0.00	0.082452
1.00	0.04286
1.50	0.01234
2.00	0.00680
2.50	0.00242

Effect of [substituents] on cooxidation rate:

The cooxidation of chalcones with substituents on benzaldehyde moiety such as *p*-CH_3, *p*-OCH_3, *p*-Cl, *p*-Br, and *p*-NO_2 groupsand chalcones having substituents on acetophenone moiety such as -*p*-CH_3, -*p*-OCH_3, - *p*-Cl, -*p*-Br, and -*p*-$NO_2$and chalcones having substituents on both moieties such as p-CH_3-p-CH_3, p-CH_3-p-Cl, p-CH_3-p-Br, p-CH_3-p-NO_2, p-Cl-p-CH_3, p-Br-p-CH_3, p-NO_2-p-CH_3, were prepared and the kinetics were conducted under pseudo-first order conditions at different temperatures (308-323 °K) to determine the various thermodynamic parameters such as $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$ and E_a.

When substituents are present in the benzaldehyde moiety of the chalcones.

The substituents such as, methyl or methoxy groups present in the para position of the benzaldehyde moiety of the chalcones enhances the rate of cooxidation. And electron-withdrawing groups like chlorine atom, bromine atom and the nitro group at the para position of the benzaldehyde moiety of the chalcones brings down the rate of the cooxidation and the retardation of the rate is more for p-NO_2 group compared with p-Cl groupand p-Br atoms (Table 4).

Table- 4: Effects of varying [reactants] on the reaction rate
I = 0.2 mol dm^{-3}; Temp: 308 K; Solvent: HOAc (50% v/v)

10^3 [CHAL] Mol dm^{-3}	10^4 [Cr(VI)] Mol dm^{-3}	10^3 [OxH_2] Mol dm^{-3}	$10^4 k_1 (S^{-1})$					
			CHAL	CHAL -OCH_3	CHAL-CH_3	CHAL -Cl	CHAL -Br	CHAL -NO_2
2	4	4	0.08245	0.6436	0.5395	0.12036	0.04265	0.001196
4	4	4	0.2047	0.8841	0.6251	0.12847	0.06458	0.003456
6	4	4	0.39012	0.9272	0.8312	0.22345	0.09495	0.005678
8	4	4	0.61153	1.2345	1.0403	0.31683	0.10346	0.007845
10	4	4	1.05224	1.6434	1.5242	0.51372	0.14042	0.012451
2	2	4	0.0428	0.1234	0.0734	0.03435	0.02581	0.000123
2	4	4	0.08245	0.2436	0.1424	0.06724	0.05445	0.000218
2	6	4	0.1845	0.4321	0.2144	0.12824	0.10245	0.002452
2	8	4	0.2436	0.7824	0.3211	0.2458	0.16824	0.006825
2	10	4	0.3210	1.3346	0.4234	0.36572	0.19846	0.012346
2	4	2	0.08245	0.9865	0.6934	0.06218	0.03815	0.000143
2	4	4	0.20125	1.4532	0.9654	0.09658	0.07248	0.000218
2	4	6	0.43216	1.8764	1.2345	0.13426	0.13286	0.000824
2	4	8	0.71886	2.2124	1.6543	0.18765	0.16843	0.001245
2	4	10	1.04956	2.6543	2.0548	0.26117	0.19087	0.00456

From the above table we noticed:
p-OCH_3 > p-CH_3 > CHAL > p-Cl >p-Br > p-NO_2

When substituents are present in the acetophenone moiety of the chalcones.
Electron-releasing groups like methoxy and methyl groups enhances the rate of cooxidation of chalcones, even if it is present at the para position of acetophenone moiety of chalcones, 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 chalcones or acetophenone moiety of the chalcones (Table 1). The chlorine substituted chalcones, and nitro group bring down the rate, the magnitude of retardation of the rate of cooxidation of (p-Chloro) chalconesand (p-Nitro) chalcones at acetophenone moiety is much more than the magnitude in the retardation of the rate of cooxidation p-Chlorochalcones and p –Nitrochalcones from that of benzaldehyde moiety.

- p-OCH_3> - p-CH_3 > CHAL > - p-Cl > -p-Br > - p-NO_2

Therefore, irrespective of the moieties at which the substituents are present, that is whether they are present at the benzaldehyde moiety of the chalcones or at the acetophenone moiety of the chalcones, 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 chalcones or acetophenone moiety of the chalcones.Therefore one can easily conclude that apart from electron–withdrawing tendency there is some other factor operating in (p-Nitro) chalconesin bringing down the rate of cooxidation.

When the same or different substituents are present in both benzaldehyde and acetophenone moiety of the chalcones.
i) When methyl groups are present at both the benzaldehyde and acetophenone moieties of chalcones, they enhance the rate of cooxidation than unsubstituted chalcones, and methyl substituted chalcones at either benzaldehyde moiety or acetophenone moiety of the chalcones.

ii) Much retardation is not at all observed if we introduce nitro group at benzaldehyde moiety of the chalcones keeping methyl group at the acetophenone moiety of the chalcones.

iii) Much retardation is observed when nitro group is introduced at the acetophenone moiety of the chalcones while whatever group is present at the benzaldehyde moiety of the chalcones.

iv)We are wonder struck to observe that if nitro groups are present at both benzaldehyde moiety of the chalcones and at acetophenone moiety of the chalcones, the retardation in cooxidation is even more.

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

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

Effect of temperature
The rate of cooxidation of chalcones and oxalic acid by Cr(VI) was measured at different temperatures(308-323 K) and the Arrhenius plot of log k_2 versus 1/T was all linear. From these plots,the Arrhenius and activation parameters were evaluated [27],[52]. (Table 5,6.Figure 4).the entropy of activation was negative and low , suggesting that the transition state is somewhat (rigid) compared to the reactant, the constancy in the values of $\Delta G^{\#}$ for the cooxidation reactions indicating that the same type of mechanism could be operative for the reaction. The isokinetic temperature was computed from Exner's plot (figure5).

Table -5: Effect of temperature on cooxidation rate
[CHAL] = 2.0 x 10 $^{-3}$moldm^{-3} ; [Cr(VI)] = 4.0 x10 $^{-4}$ mol dm^{-3} :[OxH$_2$] = 4.0 x 10 $^{-3}$mol dm^{-3} ;
I = 0.2 mol dm^{-3} ; Solvent : HOAc (50% v/v)

Substrate	10^4 k$_1$ (S^{-1})			
	308	313	318	323
CHAL	0.08245	0.15179	0.30424	0.55654
CH_3O- CHAL	0.24362	0.36546	0.48762	0.78321
CH_3- CHAL	0.12340	0.22991	0.43616	0.77021
Cl- CHAL	0.05435	0.10345	0.20584	0.36952
Br- CHAL	0.04658	0.083199	0.15225	0.30277
NO_2-CHAL	0.000218	0.000467	0.000916	0.00198
CHAL-OCH_3	0.663618	1.02345	1.82456	3.4908
CHAL-CH_3	0.539514	0.86297	1.73782	3.23592
CHAL-Cl	0.120226	0.23988	0.41304	0.83176
CHAL-Br	0.042652	0.057801	0.10964	0.26302
CHAL-NO_2	0.0011967	0.0019054	0.0038019	0.008317
CH_3- CHAL-CH_3	0.72345	1.08765	1.44692	2.17034
CH_3- CHAL-Cl	0.08654	0.12892	0.17316	0.25978
CH_3- CHAL-NO_2	0.008734	0.01432	0.01756	0.02875
Cl- CHAL-CH_3	0.097216	0.15584	0.19456	0.29457
NO_2- CHAL-CH_3	0.006723	0.01145	0.014678	0.02234

Table -6: Activation parameters: (YousifAlgamal et al. [27])
[CHAL] = 2.0 x 10 $^{-3}$moldm^{-3} ; [Cr(VI)] = 4.0 x10 $^{-4}$ mol dm^{-3} [OxH$_2$] = 4.0 x 10 $^{-3}$mol dm^{-3} ; I = 0.2 mol dm^{-3} ; Temp : 308 K ; Solvent : HOAc (50% v/v)

Substrate	10^4 k$_1$ (S^{-1})	$\Delta H^‡$ kj mol^{-1}	$-\Delta S^‡$ J deg -1 mol-^{1}	$\Delta G^‡$ kj mol^{-1}
CHAL	0.08245	46.22	165.23	50.77
CH_3- CHAL	0.12340	44.08	160.50	49.39
Cl- CHAL	0.05658	47.08	164.66	50.67
Br- CHAL	0.04658	44.66	158.70	48.84
NO_2-CHAL	0.000218	52.29	180.91	55.67
CHAL-CH_3	0.53951	43.98	179.33	55.19
CHAL-Cl	0.12022	40.65	166.20	51.15
CHAL-Br	0.042651	43.98	172.52	53.09
CHAL-NO_2	0.001197	46.72	167.94	51.68

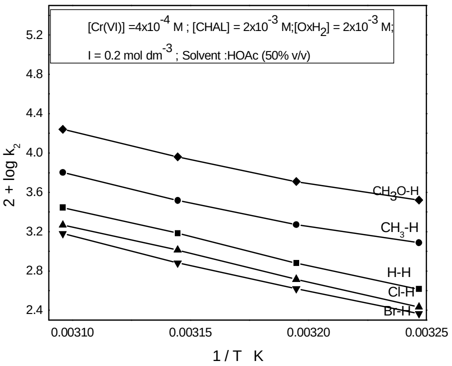

Fig.4: Arrhenius plot

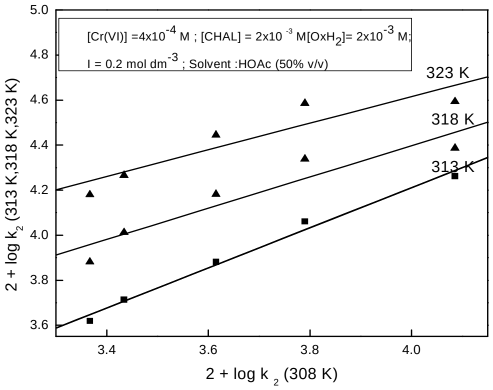

Fig.5: Exner's plot of 2 + log k$_2$ (313 K,318 K,323 K) vs 2+ log k$_2$ (308 K)

Based on the kineticsresults obtained from our previous work [27]. A suitable mechanism were proposed herein.

CONCLUSION

The rate of cooxidation of substituted chalcones and oxalic acid by chromic acid in aqueous acetic acid medium is the fractional order with respect to [substituted chalcones], the first order with respect to [Cr (VI)] and a fractional order with respect to [oxalic acid], under the experimental conditions and the chalcones is oxidized to benzaldehyde and phenyl acetaldehyde. The addition of H$^+$enhances the rate of the reaction, indicating that the protonated chalcones was more reactive in this oxidation reaction. The effect of the substituents on the reaction rate shown that the electron-releasing and electron-withdrawing groups in the benzaldehyde moiety and in acetophenonemoiety, enhancement of the rate and the retardation of the rate of cooxidation respectively. The formation of charged intermediate compound is supported by the high negative values of entropy of activation and a most probable mechanism has been proposed for cooxidation of chalcones and oxalic acid by chromic acid [27].

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