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Kinetic Investigation of Oxidation of Benzylidene Aniline by Benzimidazolium Fluorochromate

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ABSTRACT

The kinetic investigation of oxidative reaction of benzylidene aniline (BA) by benzimidazolium fluorochromate (BIFC) in the medium of 50 % acetic acid. It was catalysed by perchloric acid at 303 K ± 0.2 K. This oxidation reaction is totally exhibiting third order kinetics - first order for BIFC and second order for BA. There is no significant effect of ionic strength on the increment concentration of sodium perchlorate. There is no effect on the addition of acrylonitrile due to absence of free radical mechanism. But, the reasonable retardation in the rate of reaction for the improvement of Mn^{2+} ion, which indicates the two-electron transfer in this oxidation. From the kinetic detections, the probable mechanism cum suitable rate law is derived.

***Key words*:** Benzimidazolium fluorochromate, Benzylidene aniline, Oxidation, Mechanism, Kinetics

Kinetic studies provide rate equations to describe the speed of the reactions and attempts to detail how each chemical reaction proceed. Chemical reactions always take place in several consecutive steps which are not indicated by the stiochiometric equation, in such cases it is studied by the kinetics method and provide information regarding the equilibrium state of the reaction with complexity. The slow step is determined by the empirical formula of the activated complex in a primary reaction [1-3]. The nature of the chemical reactions and the products formed confer evidence for the mechanism involved.

The versatility of chromium compounds is slowed down the oxidation reaction while it is bounded in an aromatic ring. Numerous oxidation and reduction reactions are gaining importance due to the harmful chromium (VI) is broken into harmless chromium by changing the oxidation state. The selectivity and pacifying nature of the novel chromium (VI) oxidants have been synthesized [4-6]. The naturally occurring Chromium (VI) and Chromium (III) species differ in their biological and physio chemical activities. The benzylidene aniline and substituted benzylidene anilines were oxidized by different chromium compounds [7-15]. A less number of organic substrates were oxidized by benzimidazolium fluorochromate [16-20].

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MATERIALS AND METHODS

The oxidant BIFC [16] was first synthesized by Sivamurugan and his co-workers in the year 2005. This heterocyclic chromium (VI) oxidant is highly selective and specific in oxidizing alcohols to aldehydes or ketones respectively. The compound appears to be a yellow orange solid and the nature of the heterocyclic base is stable and less hygroscopic. It was prepared by adding chromium trioxide and benzimidazole in hydrofluoric acid in an ice bath. The solid obtained was identified with its physical properties (melting point) and further confirmed from the spectral studies.

Benzylidene aniline (BA) was prepared [10] by refluxing the equal molarity of aniline and benzaldehyde in ethanol around 2-3 hrs. The temperature of sequent concoction was reduced to room temperature with continual stirring. The yield was filtered off, drenched with ethanol and desiccated. The dried yield was again crystallized with the same solvent ethanol. The pureness of (yield) benzylidene aniline was supported by decisive its physical constant and spectral studies.

The solvent acetic acid (E Merck) was distilled by Orton and Bradfield[21] method. Perchloric acid, sodium perchlorate, acrylonitrile and manganous sulphate (E Merck) were purchased as AnalaR grade and used as such. The blank reaction was checked using these reagents properly. The aqueous reagents were prepared using double distilled water.

The oxidation reactions were preceded under pseudo-first-order conditions by the substrate concentration always in excess over that of BIFC. Notable volumes of benzylidene aniline, double distilled water and glacial acetic acid were mixed to take the percentage of acetic acid in demand value and thermostated. The reaction was started by adding the noted volume of oxidant (BIFC) to the concoction. Immediately, the minimum volume of reaction mixture was transferred into the quartz cuvette and again place it same reaction flask. It is repeated at decisive time intervals and the change in the concentration of BIFC by using digital spectrometer (ELICO CL 23 MINI SPEC) λ_{max} = 470 nm. The rate constant (psuedo-first-order) for every run was determined from the slope values obtained from the plot of log OD (absorbance) against time.

Product analysis

The reaction mixture having benzylidene aniline (0.1 M) in acetic acid solvent and benzimidazolium fluorochromate (0.1 M) in water was taken and the medium was governed using perchloric acid. The reaction mixture was subjected to warming and left aside for about two days, for the completion of the reaction and later it was extracted with ethanol, it's dark brown in colour. It is susceptible to preparative TLC through silica gel, yield two defined spots. On evaporation of solvent, the two different products are recovered to be benzaldehyde and azobenzene. It was confirmed by its spot test and spectral studies. This was in good correspondence with the literature value [22].

RESULTS AND DISCUSSION

The oxidation kinetic measurements of benzylidene aniline was followed using the benzimidazolium fluorochromate in 50% acetic acid medium. The oxidation reaction pathway is the first order dependence concerning BIFC and second order dependence concerning benzylidene aniline. Under the kinetic conditions [BA] >> [BIFC], the pseudo-first-order rate constants were determined from the linear plot of log OD (absorbance) against time (Fig 1) is linear upto 88% completion of reaction. The plot of log k_1 against log [BA] (Fig 2), reveals the reaction is second order given in the (Fig 2).

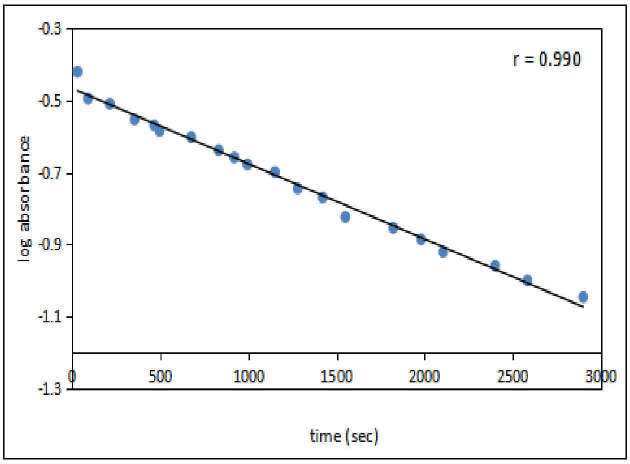


Fig 1 Plot of log (OD) absorbance against time

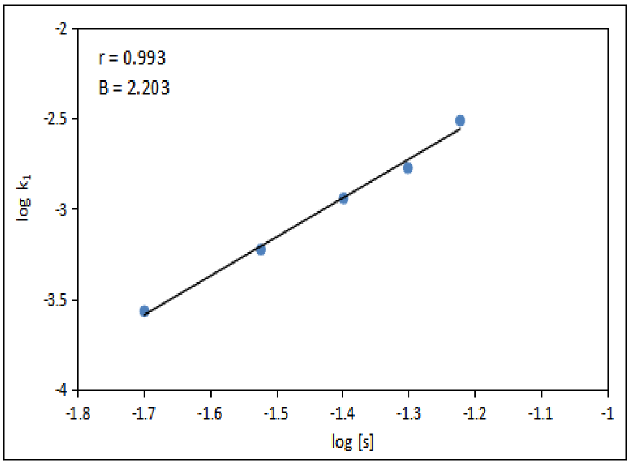


Fig 2 Plot of log k_1 against log [s]

The oxidation reaction was catalyzed by perchloric acid of different concentration. The rate constant of the reaction increased with increase in the [acid] from 0.3 to 1.5 M shown in the (Table 1). From the plot of log k_1 against log $[H^+]$ gave a straight line with good correlation coefficient, r = 0.995. The reaction is evidenced to follow fractional order kinetics since the oxidant is in the protonated form. The rate constant of the reaction had zero effect on increasing the ionic strength of the reaction medium as given in the (Table 1). This is attributed to the ionic species in the (slow step) rate determining step.

The kinetic run was conceded by changing the concentration of acetic acid and water at constant temperature (303 K). The plot of log k_1 against 1/D (dielectric constant) shown in the (Fig 4) gave a linear line with an affirmative slope value, r = 0.989, B = +54.27. This confirmed that the chromium (VI) species is involved in the slow step i.e., rate determining step [23] and the interaction is between the neutral molecule and ion.

The benzylidene aniline, acid ($HClO_4$), solvent, benzimidazolium fluorochromate were taken in a reaction flask and then added acrylonitrile, left undisturbed for a day. Absence of noticeable precipitate formed and this helps to conclude that there is no free radical formation. The rate constant of the reaction [24] (Table 1) decreased slowly with the increase in the $[MnSO_4]$ since the Mn^{2+} are implicated in the reaction by transfer of two electrons.

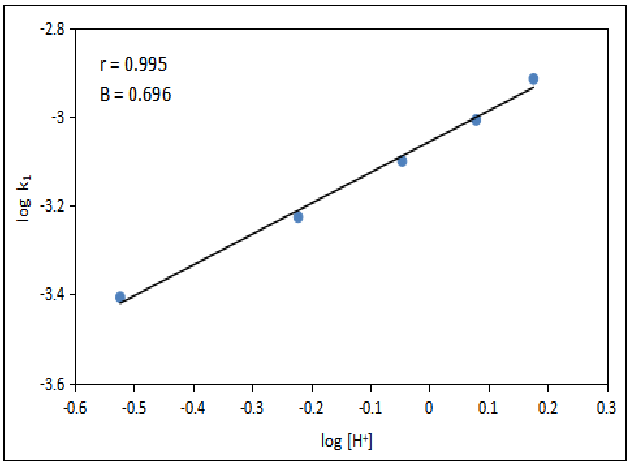


Fig 3 Plot of log k_1 against log $[H^+]$

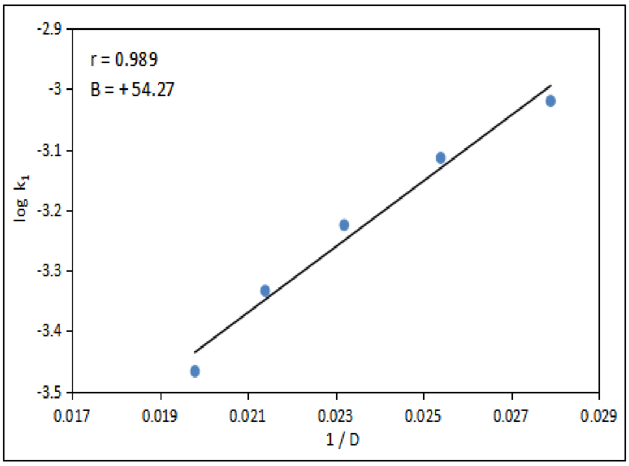


Fig 4 Plot of log k_1 against D^{-1}

Table 1 Rate data for the oxidation of benzylidene anilne by BIFC at 303 K

[BIFC]10^3 (*mol dm^{-3}*)	[BA] 10^1 (*mol dm^{-3}*)	[$HClO_4$] (*mol dm^{-3}*)	% AcOH:H_2O (v/v)	[$NaClO_4$] 10^4 (*mol dm^{-3}*)	[$MnSO_4$] 10^4 (*mol dm^{-3}*)	k_1 10^4 (*s^{-1}*)
1.0	3.0	0.6	50:50	-	-	6.02
1.5	3.0	0.6	50:50	-	-	6.11
2.0	3.0	0.6	50:50	-	-	5.96
2.5	3.0	0.6	50:50	-	-	5.88
3.0	3.0	0.6	50:50	-	-	6.06
2.0	2.0	0.6	50:50	-	-	2.71
2.0	3.0	0.6	50:50	-	-	5.96
2.0	4.0	0.6	50:50	-	-	11.46
2.0	5.0	0.6	50:50	-	-	18.92
2.0	6.0	0.6	50:50	-	-	30.83
2.0	3.0	0.3	50:50	-	-	3.93
2.0	3.0	0.6	50:50	-	-	5.96
2.0	3.0	0.9	50:50	-	-	7.96
2.0	3.0	1.2	50:50	-	-	9.86
2.0	3.0	1.5	50:50	-	-	12.22
2.0	3.0	0.6	40:60	-	-	3.41
2.0	3.0	0.6	45:55	-	-	4.63
2.0	3.0	0.6	50:50	-	-	5.96
2.0	3.0	0.6	55:45	-	-	7.69
2.0	3.0	0.6	60:40	-	-	9.55
2.0	3.0	0.6	50:50	2.5	-	5.90
2.0	3.0	0.6	50:50	5.0	-	6.04
2.0	3.0	0.6	50:50	7.5	-	5.99
2.0	3.0	0.6	50:50	10.0	-	6.11
2.0	3.0	0.6	50:50	-	2.5	4.02
2.0	3.0	0.6	50:50	-	5.0	3.84
2.0	3.0	0.6	50:50	-	7.5	3.41
2.0	3.0	0.6	50:50	-	10.0	3.22

This oxidation reaction of benzylidene aniline was dependent to the temperatures like 298 K, 303 K, 308 K, 313 K and 318 K by having other parameters as constant. From the Eyring's least square method, thermodynamic and activation parameters [25] was assessed. The reaction rate constants were raised with ascent in the temperature (Table 2). The plot of log k_2/T against 1/T gave a straight line as shown in the (Fig 5).

Table 2 Effect of temperature for the oxidation of benzylidene Anilne by BIFC

Temperature (K)	k_1 10^5 (s^{-1})	Thermodynamic and activation parameters
298	4.57	$\Delta H^{\#}$ = 16.62 *kJ mol^{-1}*
303	5.96	$\Delta S^{\#}$ = -177.42 *J K^{-1} mol^{-1}*
308	8.02	$\Delta G^{\#}$ = 70.38 *kJ mol^{-1}* at 303 K
313	10.25	Ea = 19.14 *kJ mol^{-1}* at 303 K
318	12.72	-

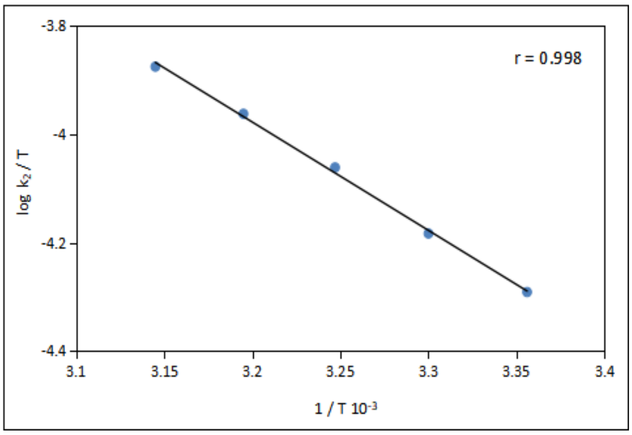
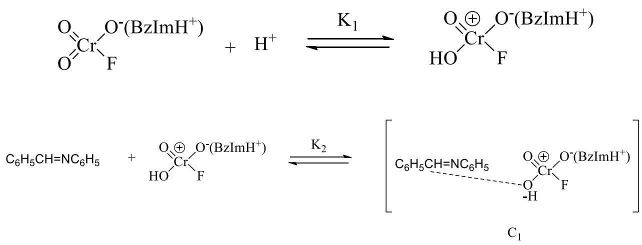
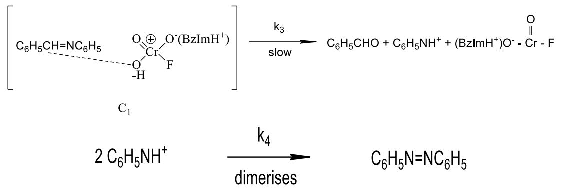


Fig 5 Eyring's plot of log k_2/T against T^{-1}

Mechanism

From the kinetic reference points prove that, BIFC concerning first order dependence and BA concerning second order dependence and catalysed by perchloric acid. The medium (CH_3COOH + H_2O) prove to be important role in this oxidation reaction. The effect of solvent composition and sodium perchlorate carried out and favours the reaction. Absence of noticeable precipitate formed and this helps to conclude that there is no free radical formation. But, the noticeable catalytic effect, the rate of reaction decreased slowly with the increase in the [$MnSO_4$]. The two different products are recovered from product analysis i.e., benzaldehyde and azobenzene (Scheme 1).





Rate law

Rate $= k_3$ [Complex]

$= k_3K_2[S][BIFCH^+]$

$= k_3K_2K_1[S][BIFC][H^+] / (1+K_1[H^+])$ -d[BIFC] / dt

$= k_3K_2K_1[S]^2[BIFC][H^+] / (1+K_1[H^+])$

The projected mechanism and desirable rate law supports all the kinetic results and including the solvent effect, the negative value of entropy.

CONCLUSION

This investigated study, the oxidation mechanism of benzylidene aniline by benzimidazolium fluorochromate. The order of reaction is one concerning BIFC, two concerning benzylidene aniline and it was catalysed by perchloric acid. From the kinetic data obtained, the thermodynamic and activation parameters have been calculated using Eyring's equation. A probable mechanism and suitable rate law also derived.

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