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Hammett Plot Behaviour of Substituted Benzaldehydes Towards Piperidinium Chlorochromate Oxidation

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ABSTRACT

The conversion of benzaldehydes to the corresponding benzoic acids was performed in an equivalent mixture of acetic acid and water. This oxidation kinetics was followed by the spectrophotometric method. The orders concerning benzaldehydes and oxidant were both one and fractional order concerning perchloric acid. The substituent effect of rate of reaction was analyzed by employing various *meta*- and *para*-substituted benzaldehydes. The rate of reaction was increased concerning electron-releasing groups and decreased concerning electron-removal groups. The excellent linear Hammett plot behaves with negative ρ-values, it supports the role of chromate ion intermediate in the slow step of the mechanism. The produced intermediate state is established to be rigid as the negative value of entropy. The values of change in free energy ($\Delta G^{\#}$) are found to the nearly constant and this designates all the substituted benzaldehydes follows a common mechanism.

Key words: Benzaldehydes, Piperidinium chlorochromate, Oxidation, Hammett plot, Spectrophotometry

The applications of benzaldehydes in the field of organic synthesis is very wide such as oxidation, reduction, bromination and more applications. The oxidation of alcohols and aldehydes is studied in various works [1-2]. Piperidinium chlorochromate [3] is a mild oxidant under chromium (VI) compounds. It is used for various organic oxidation reactions. Some of the benzaldehydes has been oxidised with different chromium (VI) compounds as kinetic and mechanistic aspects [4-12]. Oxidation of substituted benzaldehydes by piperidinium chlorochromate contains perchloric acid is our new attempt.

MATERIALS AND METHODS

Piperidinium chlorochromate (PipCC) was prepared using a reported procedure [3]. Benzaldehydes and all other chemicals were purchased from Sigma Aldrich with AnalaR grade. The liquid benzaldehydes under vacuum distillation can be used. The solution was prepared by using double distilled water only.

Kinetic measurements

A substrate concentration is more when compared to oxidant (i.e., pseudo-first-order condition) for this oxidation reaction proceeds kinetically. The reactions were carried out for 80% completion with the same temperature (± 0.1 K). The unreacted piperidinium chlorochromate was estimated spectrophotometrically. The rate constants were determined by the linear least-square plot between log absorbance and time.

Correlation analysis

The Micro cal origin computer software used for Linear regression (r) analysis. The results have reproducible and the rate constants were approximately ± 2%.

Stoichiometry and product analysis

Stoichiometric studies showed that equal mole of benzaldehydes and piperidinium chlorochromate consumed (1 mole) which gives the corresponding benzoic acids. Benzaldehydes and piperidinium chlorochromate were mixed with perchloric acid in 50% aqueous acetic acid (total 100 ml). This reaction mixture was warmed gently and then maintained at room temperature for about 24 h to confirm the completion of the reaction. This mixture was infused with ether, the ether layer was dried with dried sodium sulphate. The product was known by assay its physical constant (m.p. 120ºC) with spectral studies. The yield was calculated to be around 93%.

RESULTS AND DISCUSSION

Benzaldehydes being taken in large extra, the linear plot between log absorbance and time indicates first-order dependence on [PipCC] and also the first-order rate

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constants decrease with an increase [PipCC]. It is due to the decrement in the strength of Cr (VI) species effective in the oxidation reaction [13]. The rate of reaction rises linearly with a rise in the concentration of benzaldehydes. The linear plot between log k_1 and log [s] with slope (0.974 - 1.192) for almost all the substituted benzaldehydes. The concentration of perchloric acid changes from 0.2 to 0.6 molar in the reaction mixture, the rate of reaction steadily increased (Table 1). The slope of the linear plot between log k_1 and log $[H^+]$ gives 0.340, it shows that the effective nature of protonated species in the oxidant. With these observations, the oxidation reaction makes simply an acid-catalyzed [14] one.

The rate of oxidation is not affected by varying the ionic strength in the addition of sodium perchlorate. The proportion of the acetic acid increase in the solvent mixture rises the rate of reaction with a slope (+ 30.17) having a positive value for the plot between log k_1 and 1/D. The free radical formation has been tested with acrylonitrile and it clearly indicates no free radical mechanism in this kinetics. The reaction rate retards by the gain of manganous sulphate which conforms two-electron process in the reaction. The product has been confirmed by the IR and mass spectrum. Such shreds of evidence have been already reported in the oxidation of benzaldehyde by piperidinium chlorochromate [15].

Table 1 Rate data for oxidation of benzaldehyde by PipCC at 303 K

[Benzaldehyde] 10^2 (*mol dm^{-3}*)	[PipCC] 10^3 (*mol dm^{-3}*)	$[H^+]$ (*mol dm^{-3}*)	$[NaClO_4]$ 10^3 (*mol dm^{-3}*)	AcOH : Water (*v/v*)	$[MnSO_4]$ 10^3 (*mol dm^{-3}*)	k_1 10^4 (*s^{-1}*)
4.5 - 10.5	3.0	0.2	0.0	50:50	0.0	14.322 - 39.445
6.0	2.0 - 6.0	0.2	0.0	50:50	0.0	21.770 - 13.305
6.0	3.0	0.2 - 0.6	0.0	50:50	0.0	19.924 - 29.444
6.0	3.0	0.2	0.0 - 8.0	50:50	0.0	19.924 - 19.905
6.0	3.0	0.2	0.0	40:60 - 60:40	0.0	15.345 - 26.994
6.0	3.0	0.2	0.0	50:50	0.0 - 8.0	19.924 - 14.555

Mechanism and rate law

From the experimental evidence so far and the report of previous work with chromic acid oxidation [16-17]; the two-electron movement with chromium (IV) formation. The state of chromium ion participation in the reaction has been proved with the addition of manganous sulphate. Benzaldehyde and its derivatives follow first order which results from the linear plot of log k_1 against log [s] (Fig 1-2). The graph has a slope nearly unity and follows a common mechanism.

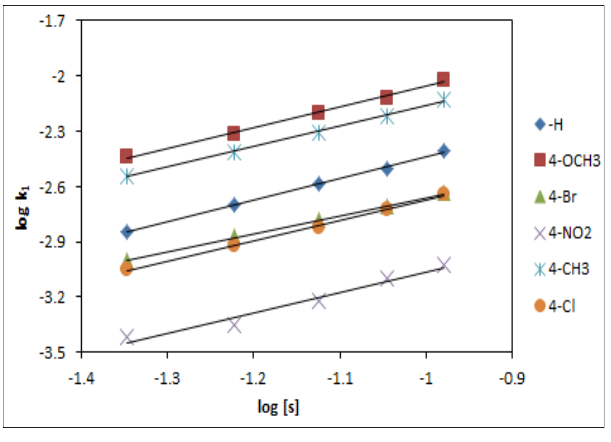


Fig 1

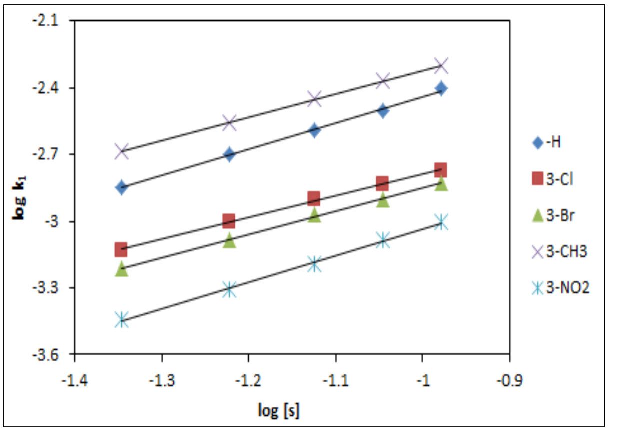
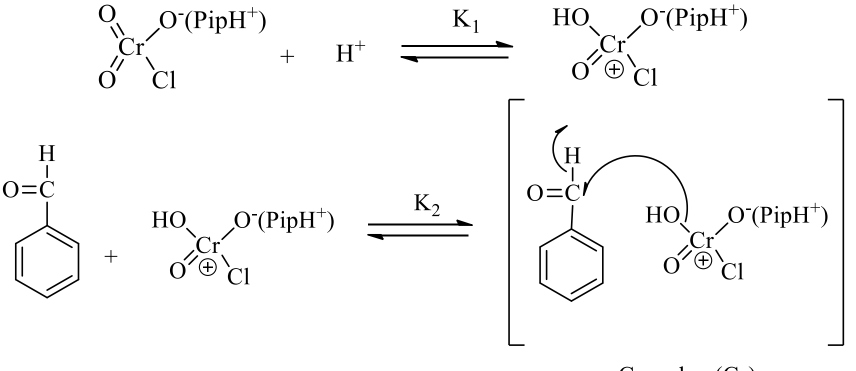


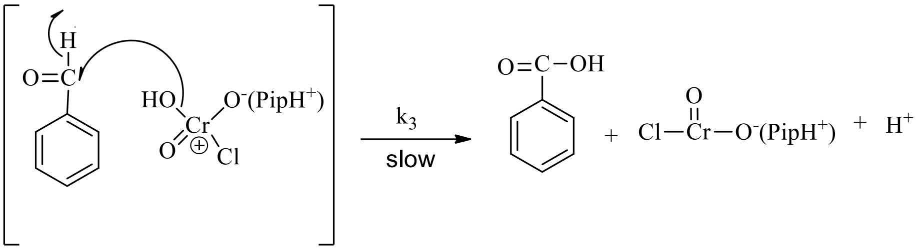
Fig 2

Fig 1-2 Substrate effect plot

Mechanism



Complex (C_1)



Complex (C_1)

Rate Law

$$\text{Rate} = k_3\,[\text{Complex}]$$
$$= k_3K_2\,[\text{PipCCH}^+][S]$$
$$= k_3K_2K_1\,[\text{PipCC}][S][H^+] / 1 + K_1[H^+]$$
$$-d\,[\text{PipCC}]/dt = k_{obs}[\text{PipCC}][S][H^+] / 1 + K_1[H^+]$$

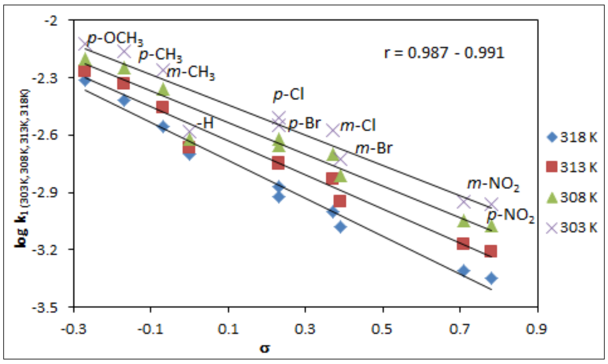


Fig 3 Hammett plot

Effect of substituents

The rate of oxidation has been studied for the effect of substituents on *para-* and *meta*-position of benzaldehydes. The electron-releasing groups rise reaction rate and electron-withdrawing groups retards reaction rate. Electron-releasing substituents form a transition state with a carbonium ion centre which enhance the bond-breaking in the same step by resonance. Electron-retreating substituents increase the ability of the carbocation centre, which represents the evolution of losses at the transition state. This leads to assist the bond-making process which in turn decreases in the rate of reaction.

For all the substituted benzaldehydes of rate data were determined from 303 K to 318 K. Based on Eyring's equation, the plot of log k_2/T against 1/T can be derived and entropy, enthalpy, free energy and energy of activation were calculated. A Hammett plot [18] of log $k_{1(303K,\ 308K,\ 313K,\ 318K)}$ against σ was drawn (Fig 3) to structure-reactivity correlation. The negative ρ values [19-20] indicates the lack of electron-rich transition state and are more pronounced with the increase in temperature. It was evident that the active role of chromate ion intermediate in the rate-determining step.

The transition state formed established to be rigid as the entropy of activation values ($\Delta S^{\#}$) are negative (Table 2). The reduction in the degree of freedom in the molecules was observed as a result of a negative value. The data interpretation has been made in accordance with the linear free energy relationship for this oxidation process. The low values of change in the enthalpy of activation ($\Delta H^{\#}$) and E_a propose the concerted mechanism. The difference in $\Delta S^{\#}$ should be linearly related to the variation in $\Delta H^{\#}$ [21]. The resultant straight line (Figure 4) with a good correlation coefficient (r = 0.991) has arrived from the linear isokinetic plot. From the slope of the isokinetic plot, it was observed that the isokinetic temperature was 335.9 K. Since, the β value is higher than the experimental temperature; it indicates that this oxidation reaction is enthalpy-controlled reaction [22]. The values of change in free energy ($\Delta G^{\#}$) are found to the nearly constant and this designates all the substituted benzaldehydes follows a common mechanism. A straight line with an excellent correlation was obtained from the plot of log $k_{1(308K,\ 313K,\ 318K)}$ against log $k_{1\ (303\ K)}$ (Fig 5). This good correlation specifies that all the substituted benzaldehydes follow a common mechanism.

Table 2 Some parameters for the oxidation of benzaldehydes by PipCC

Substituents	Order w.r.to [S]	k_1 x 10^4 (s^{-1}) 303 *K*	308 *K*	313 *K*	318 *K*	$\Delta H^{\#}$ (*kJ mol*$^{-1}$)	(-) $\Delta S^{\#}$ (*JK*$^{-1}$ *mol*$^{-1}$)	$\Delta G^{\#}$ at 308 *K* (*kJ mol*$^{-1}$)	E_a at 308 *K* (*kJ mol*$^{-1}$)	r
-H	1.181	19.924	21.615	23.827	26.318	5.36	212.78	69.83	7.88	0.997
p-OCH_3	1.121	48.417	54.211	63.147	75.041	9.14	197.17	68.88	11.66	0.993
p- CH_3	1.112	38.371	46.461	56.172	69.313	12.56	186.68	69.12	15.08	0.999
p-Br	0.974	13.428	17.727	22.142	28.221	15.92	179.32	70.25	18.44	0.999
p-Cl	1.110	11.967	17.884	23.914	31.117	20.93	163.12	70.35	23.45	0.995
p-NO_2	1.115	4.456	6.187	8.422	10.927	19.79	170.53	71.46	22.31	0.999
m-CH_3	1.042	27.925	35.111	44.079	55.118	14.70	180.76	69.47	17.22	0.999
m-Br	1.041	8.279	11.332	15.442	18.821	18.21	173.46	70.77	20.73	0.995
m-NO_2	1.192	4.920	6.722	8.975	11.224	18.16	175.54	71.35	20.68	0.998
m-Cl	0.978	9.908	14.721	19.927	26.777	21.78	161.01	70.57	24.30	0.997

[PipCC] = 3.0 x 10^{-3} *mol dm*$^{-3}$ AcOH : H_2O = 50:50 *(v/v)* [Benzaldehyde] = 6.0 x 10^{-2} *mol dm*$^{-3}$ [H^+] = 0.2 *mol dm*$^{-3}$

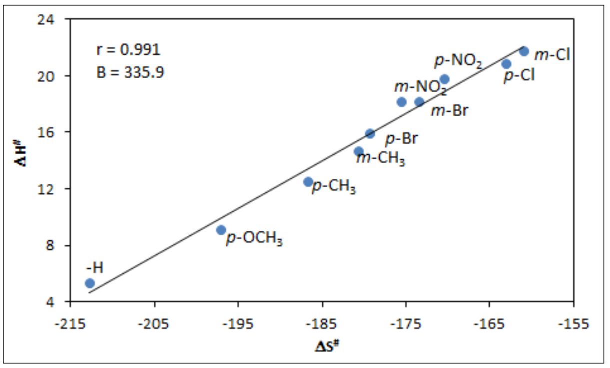


Fig 4 Isokinetic plot

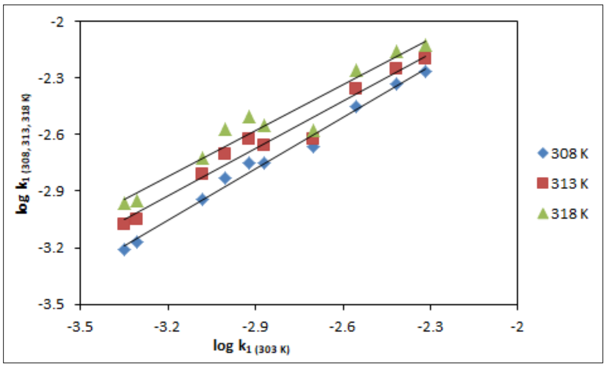


Fig 5 Exner's plot

The proposed mechanism for these studies in relation with the rate law and support all the observations

CONCLUSION

Oxidation of substituted benzaldehydes by piperidinium chlorochromate in the mixture of water and acetic acid yields the corresponding benzoic acids as the final product. The proposed mechanism for this oxidation is by the observed experimental evidence. The isokinetic temperature was determined from the slope of the linear isokinetic plot. An excellent correlation is obtained from the linear Exner's plot. This suggests that all the substituted benzaldehydes follow a unique mechanism. A Hammett plot was drawn to correlate structure-reactivity for these reactions.

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