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Kinetic Study on Imidazolium Dichromate Oxidation of benzyl alcohols – Non linear Hammett's Plot

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ABSTRACT

Imidazolium dichromate (IDC) oxidizes benzyl alcohol and substituted benzyl alcohols have been studied in aqueous acetic acid and in the presence of acid to the corresponding aldehydes. The reaction was carried out under pseudo-first order conditions. The reaction has unit dependence on each of the benzyl alcohol and IDC. The reaction is catalyzed by hydrogen ions. The decrease in dielectric constant of the medium increases the rate of the reaction. Electron-withdrawing substituent on benzyl alcohol reduces the rate of oxidation, while electron-donating group enhances the rate compared to the unsubstituted benzyl alcohol. However, correlation of the logarithm of the rate constant with the Hammett's substituent constant σ gives a smooth curve. This is explained due to the operation of substituent effect on two steps of the mechanism proposed.

Keywords: Kinetics, Oxidation, Benzyl Alcohol, Imidazolium dichromate.

INTRODUCTION

Benzyl alcohols are used emulsions and ointments and in lotions for the relief of insect bites . Other applications for benzyl alcohol include cosmetics and personal care formulations as well as coatings and lacquers. Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compound [1]. Numerous reagents and experimental procedures have been developed to carry out this transformation [2], in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds [3-4]. Imidazolium dichromate has been used as a mild selective oxidant in synthetic organic chemistry [5]. The kinetics and mechanism of oxidation of benzyl alcohols have been studied for number of oxidizing agents, such as quinolinium chlorochromate [6], quinolinium flurochromate [7], benzimidazolium flurochromate [8], pyridinium fluorochromate [9-10], isoquinolinium bromochromate [11], morpholinium chlorochromate [12] and

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tripropylammonium fluorochromate [13] under different experimental conditions. It appears that no work has yet been done on their oxidation of benzyl alcohols by imidazolium dichromate (IDC) from a kinetic view point. Attempts have been made to correlate rate and structure in such a reaction.

EXPERIMENTAL SECTION

Imidazolium dichromate (IDC) was prepared by the reported method [5] and its purity checked by an iodometric method. Benzyl alcohol (Aldrich) and substituted benzyl alcohols were used as such after a check of its physical constants. Acetic acid was refluxed over chromium trioxide for 6hr and then fractionated [14]. Triply distilled water was used throughout the kinetic runs.

Kinetic Measurements :

All the kinetic experiments were conducted under pseudo-first order conditions ([BzOH] >> [IDC]) in 50% (v/v) aqueous acetic acid at 0.03 $mol\ dm^{-3}$ in H_2SO_4. The progress of the reaction was followed by estimating the unreacted imidazolium dichromate (IDC) at regular time intervals. The reactions were carried out at constant temperature (±0.1K) and followed by spectrocolorimetrically. The rate constants were evaluated from the linear plot log absorbance against time by least square method, were reproducible to within ±3%. The activation parameters were calculated from the slope and intercept of linear plot of ln (k_1/T) against 1/T employing the Eyring's equation.

Product analysis:

The reaction mixture with excess of oxidant after slight warming was kept for 24hr, extracted with chloroform and the organic layer was washed with water, dried over anhydrous sodium sulphate. The product benzaldehyde were identified by the formation of 2,4-dinitro phenyl hydrazone (m.p. 235^{o}C, lit.237^{o}C) and spectral studies.

RESULTS AND DISCUSSION

The first order dependence of the reaction of benzyl alcohol on imidazolium dichromate is obvious from the linearity of the plot of log [IDC] *versus* time over 70% of the reaction. At higher concentrations of the oxidant, the rate constants are decreased with increasing oxidant concentration. This observation is well explained by Wiberg [15]. With the increase of the concentration of Cr(VI) a progressively smaller portion of the total amount is in the form of monomeric Cr(VI) ion and hence the rate constants are decreased with increasing Cr(VI) concentration.

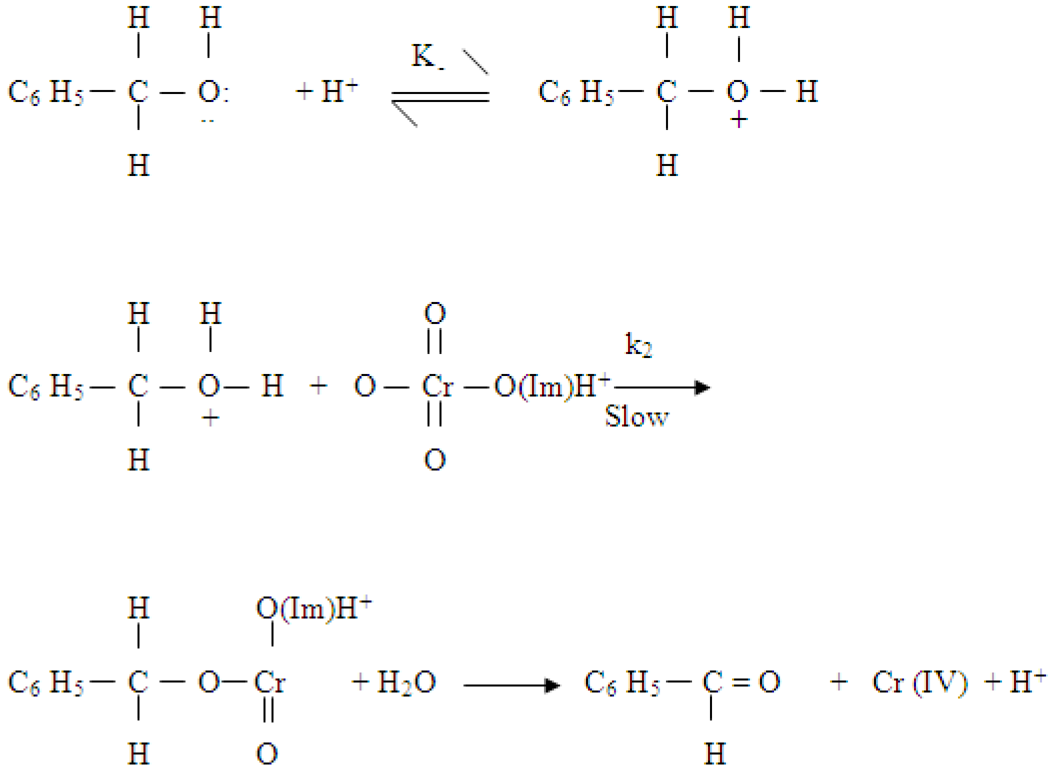
The reaction was found to be first-order in substrate as evident by the unit slope (r=0.998) of the plot of log k_1 *versus* log [BzOH]. The effect of acidity was studied by varying the concentration of sulphuric acid and the rate constants were found to be increasing with the increase in the concentration of sulphuric acid. But the plot of log k_1 *versus* log $[H^+]$ do not give an ideal slope of unity which indicate simply that the reaction is and acid catalyzed one (Table 1).

The effect of solvent composition on the rate of oxidation has been studied by determining the k_1 values in aqueous acetic acid of different compositions in the range 40% - 70% (v/v). These values increases with increase in the proportion of acetic acid in the medium, indicating that, a medium of low dielectric constant (D) is more favourable for the oxidation process. Further, the plot of log k_1 *versus* 1/D is linear with a slope of +45.0. Change in ionic strength of the medium using added sodium sulphate has negligible effect on rate (Table 2). These two observations pointed out to an ion-dipole type of interaction between the oxidant and substrate [16-17].

Table 1. Effect of variation of [IDC], [BzOH] and [H_2SO_4] on the rate of oxidation of Benzyl alcohol with imidazolium dichromate(IDC)
Solvent = 50% AcOH – H_2O; Temperature = 313K

[IDC] 10^3 *mol dm^{-3}*	**[BzOH] 10^2** *mol dm^{-3}*	**[H_2SO_4] 10^2** *mol dm^{-3}*	**$k_1 \times 10^4$** *s^{-1}*
3.24	5.00	2.48	2.26
4.32	5.00	2.48	1.80
5.40	5.00	2.48	1.48
6.48	5.00	2.48	1.29
7.56	5.00	2.48	1.82
4.92	2.50	2.48	0.80
4.92	7.50	2.48	3.04
4.92	10.00	2.48	3.82
4.92	12.50	2.48	5.06
4.92	5.00	4.95	2.75
4.92	5.00	7.43	4.17
4.92	5.00	9.91	5.75
4.92	5.00	12.38	7.58
4.92	5.00	14.86	8.71

Mechanism:



Scheme – I

The reaction mixture, when allowed to stand with acrylonitrile does not induce polymerisation, suggesting the absence of free radical mechanism. On the other hand, the addition of Mn^{2+} ions retarded the reaction rate showing the two electron transfer process in the reaction (Table 2).

Taking all these observations into consideration the possible mechanism of oxidation can be written as shown in Scheme - I.

The rate law derived from the above mechanism (Scheme I) is

$$-\frac{d[IDC]}{dt} = K\,k_2\,[BzOH]\,[IDC]\,[H^+]$$

The proposed mechanism and the derived rate law fit well to the experimental observations.

Table 2. Effect of dielectric constant, ionic strength and $MnSO_4$ on the reaction rate
[IDC] = 4.92×10^{-3} *mo1dm*$^{-3}$; [BzOH] = 5.00×10^{-2} *mo1dm*$^{-3}$; Temperature = 313*K*

Percentage of acetic acid (v/v)	$k_1 \times 10^4$ s^{-1}	$[Na_2SO_4]\ 10^4$ *mo1dm*$^{-3}$	$k_1 \times 10^4$ s^{-1}	$[MnSO_4]\ 10^4$ *mol dm*$^{-3}$	$k_1 \times 10^4$ s^{-1}
40	1.10	0.00	1.80	0.00	1.80
50	1.80	5.00	1.84	5.00	1.68
60	2.72	10.00	1.78	10.00	1.57
70	5.75	15.00	1.82	15.00	1.42
-	-	20.00	1.76	20.00	1.30

Effect of substituents on the reaction rate.

The rate of oxidation of some substituted benzyl alcohols has been studied at four different temperatures, viz., 303K, 313K, 323K and 333K. The thermodynamic parameters are calculated using the Eyring's plot [18] and the values are given in Table 3. The negative values of the entropy of activation ($\Delta S^\#$) suggest extensive salvation of the transition state over the reactants. The enthalpy of activation ($\Delta H^\#$), values are very low suggesting a concerted mechanism as proposed. As $\Delta H^\#$ and $\Delta S^\#$ do not vary linearly, no isokinetic relationship is observed. This indicates the absence of enthalpy - entropy compensation effect [19]. Exner [20] criticized the validity of such linear correlation between $\Delta H^\#$ and $\Delta S^\#$ as these quantities are dependent on each other. When the measurements at two different temperatures (303K and 323K) have been made. The data can be analyzed with the following equation [21].

$$\log k_1 (T_2) = a + b \log k_1 (T_1) \qquad \text{where } T_2 > T_1$$

The plot of $\log k_{1(323K)}$ versus $\log k_{1(303K)}$ gives a straight line with r=0.996,such a good correlation indicates a unified mechanism with all the benzyl alcohols studied.

Table 3. Thermodynamic parameters for the oxidation of *para*- and *meta*-benzyl alcohols by imidazolium dichromate(IDC)
[BzOH] = 5.00×10^{-2} *mo1dm*$^{-3}$ [IDC] = 4.92×10^{-3} *mo1dm*$^{-3}$
[H_2SO_4] = 2.48×10^{-2} *mo1dm*$^{-3}$ AcOH-H_2O =50% (v/v)

Sl. No.	**Substituent**	**$k_1 \times 10^4$ s^{-1}**				**$\Delta H^\#$** *kJmo1*$^{-1}$	**$-\Delta S^\#$** *JK*$^{-1}$*mo1*$^{-1}$
		303*K*	**313*K***	**323*K***	**333*K***		
1.	BzOH	1.38	1.80	2.12	2.86	17.25	237.32
2.	*p*-CH_3	2.96	3.98	6.05	9.31	29.53	204.54
3.	*m*-CH_3	1.84	2.82	4.81	6.76	34.36	178.42
4.	*p*-OCH_3	5.76	7.08	9.76	13.08	20.99	213.38
5.	*p*-C1	0.92	1.20	1.90	2.88	29.83	199.58
6.	*m*-C1	0.68	1.12	1.82	2.62	35.52	182.72
7.	*p*-Br	0.76	1.08	1.74	2.46	30.89	197.36
8.	*m*-Br	0.63	0.94	1.38	2.20	32.13	194.88
9.	*p*-NO_2	0.50	0.74	1.78	2.52	30.70	201.43
10.	*m*-NO_2	0.48	0.68	1.62	2.44	23.20	226.33

The plot of log k_1 *versus* Hammett's substituent constant [22] (σ) gives a smooth curve as shown in Fig.1. This is explained as follows: In the present system, the substituent influences two steps of the mechanism, (i) the equilibrium protonation of benzyl alcohol and (ii) the attack of the oxidant on the carbonium ion. Electron - releasing groups on the benzyl alcohol enhances the case of protonation, compared to the unsubstituted one, while electron - withdrawing groups facilitate the attack of the oxidant and the formation of the ester, compared to the unsubstituted one.

In this case, the shape of the smooth curve, the effect of substituent on k_1, the protonation constant, is more than that of k_2, the rate constant of the slow step.

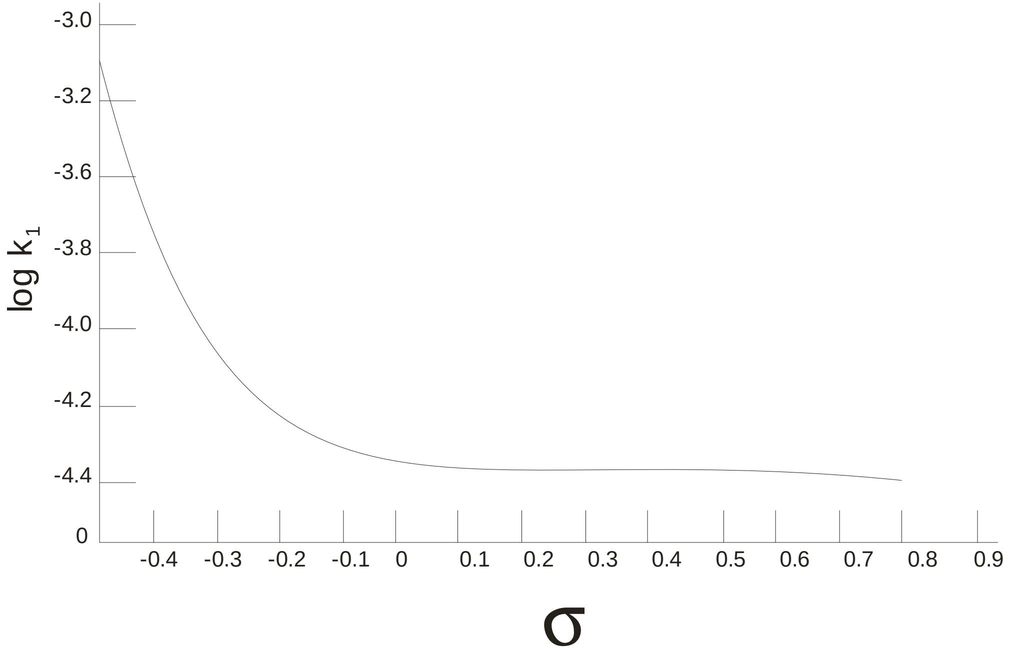


Fig.1 – Hammett's Plot

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