



# Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Imidazolium Dichromate in Aqueous Acetic Acid Medium

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Received 16 March 2009; Accepted 10 May 2009

**Abstract:** The kinetics of oxidation of benzaldehyde (BA) and *para*-substituted benzaldehydes by imidazolium dichromate (IDC) has been studied in aqueous acetic acid medium in the presence of perchloric acid. The reaction is first order each in [IDC], [Substrate] and  $[H^+]$ . The reaction rates have been determined at different temperatures and the activation parameters calculated. Electron withdrawing substituents are found to increase the reaction and electron releasing substituents are found to retard the rate of the reaction and the rate data obey the Hammett relationship. The products of the oxidation are the corresponding acids. The rate decreases with the increase in the water content of the medium. A suitable mechanism is proposed.

**Keywords:** Benzaldehyde, Kinetics and Mechanism, Oxidation, Imidazolium dichromate,

## Introduction

A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizable functional group<sup>1</sup>. A number of new chromium(VI) containing compounds, with heterocyclic bases, like pyridinium chloro chromate(PCC)<sup>2</sup>, pyridinium bromo chromate (PBC)<sup>3-5</sup>, quinolinium chloro chromate(QCC)<sup>6,7</sup>, quinolinium fluoro chromate(QFC)<sup>8</sup>, quinolinium bromo chromate(QBC)<sup>9</sup>, imidazolium fluorochromate(IFC)<sup>10</sup>, pyridinium fluoro chromate (PFC)<sup>11-14</sup>, imidazolium dichromate(IDC)<sup>15</sup> and quinolinium dichromate(QDC)<sup>16</sup> have been developed to improve the selectivity of oxidation of organic compounds. The kinetics and mechanism of oxidation of aromatic aldehydes by various oxidants have been reported<sup>17-19</sup>. However,

the kinetics of oxidation of substituted benzaldehydes by IDC, a Cr(VI) reagent has not yet been studied. This prompted us to undertake the present investigation. The present work reports the kinetics of oxidation of *para*-substituted benzaldehydes by IDC and evaluates the reaction constants. Mechanistic aspects are also discussed.

## Experimental

All benzaldehydes used were of AnalaR Grade (E Merck, Germany), the solid benzaldehydes were used as such and the liquid benzaldehydes were used after vacuum distillation. The oxidant imidazolium dichromate (Aldrich) was used. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

### *Kinetic measurements*

The reactions were followed under pseudo-first-order conditions by maintaining a large excess ( $\times 15$  or greater) of the benzaldehyde over IDC. The temperature was kept constant to  $\pm 0.1$ K. The reactions were followed by monitoring the decrease in the concentration of IDC spectrophotometrically at 363 nm by using Shimadzu U.V /Visible spectrophotometer with recording facilities for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants,  $k_{obs}$ , were evaluated from the linear plots of  $\log [\text{IDC}]$  against time. Duplicate kinetic runs showed that the rate constants were reproducible to within  $\pm 4\%$ .

### *Product analysis*

Product study was made under mineral acid catalysed conditions in benzaldehyde. Keeping concentration of IDC in excess over benzaldehydes, the two solutions were mixed and perchloric acid was also added in 50% acetic acid -50% water mixtures. The reaction mixture was set aside for about 24h to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was then kept on a water bath for the evaporation of ether and cooled in ice bath to obtain the product (m.p.121 °C). The product was dissolved in benzene and a careful TLC analysis was done with benzoic acid and benzaldehyde as references. Only one spot corresponding to benzoic acid was obtained. Formation of benzoic acid was further confirmed by mixing the product with pure benzoic acid and noting that there was no change in the melting point.

### *Stoichiometric studies*

Stoichiometric analysis showed that 3 mol of aldehyde consumed 2 mol of IDC in accordance with Eq (1) to give the corresponding carboxylic acid.



## Results and Discussion

Oxidation of benzaldehyde by IDC has been conducted in 50% acetic acid - 50% water medium at 303 K, under the pseudo-first-order conditions and the observed results were discussed in the following pages.

### *Effect of varying oxidant concentration*

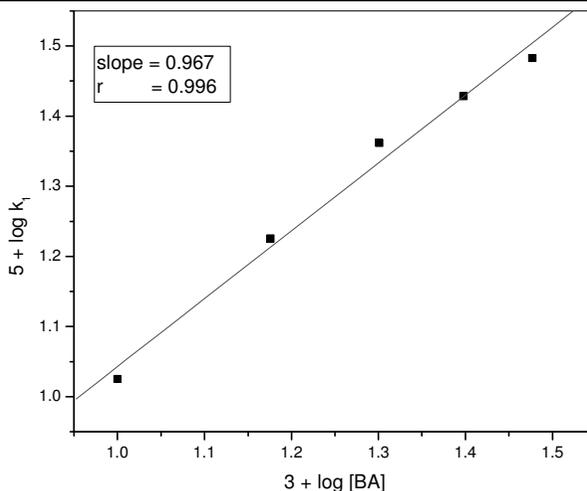
The concentration of IDC was varied in the range  $6.00 \times 10^{-4}$  to  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup> and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The near constancy in the value of  $k_1$  irrespective of the concentration of the IDC confirms the first order dependence on IDC.

*Effect of varying substrate concentration*

The substrate benzaldehyde was varied in the range of  $1.00 \times 10^{-2}$  to  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup> at 303 K and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of benzaldehyde, indicating first order dependence with substrate. The plot of  $\log k_{\text{obs}}$  versus  $\log [\text{BA}]$  gave the slope of 0.967 ( $r = 0.996$ ) (Figure 1) shows that this oxidation reaction was first order with respect to [BA]. The second order rate constant  $k_2$  is invariant supporting the first order dependence on [BA].

**Table 1.** Effect of varying [BA], [IDC] and [HClO<sub>4</sub>] on the rate reaction at 303 K AcOH – H<sub>2</sub>O = 50% - 50% (v/v)

[BA] 10 <sup>2</sup> mol.dm <sup>-3</sup>	[IDC] 10 <sup>3</sup> mol.dm <sup>-3</sup>	[HClO <sub>4</sub> ] mol.dm <sup>-3</sup>	$k_{\text{obs}} 10^4$ s <sup>-1</sup>
1.0	1.2	0.40	1.06
1.5	1.2	0.40	1.68
2.0	1.2	0.40	2.30
2.5	1.2	0.40	2.68
3.0	1.2	0.40	3.18
2.0	0.6	0.40	2.26
2.0	1.8	0.40	2.18
2.0	2.4	0.40	2.20
2.0	3.0	0.40	2.16
2.0	1.2	0.20	1.04
2.0	1.2	0.30	1.62
2.0	1.2	0.50	2.70
2.0	1.2	0.60	3.20

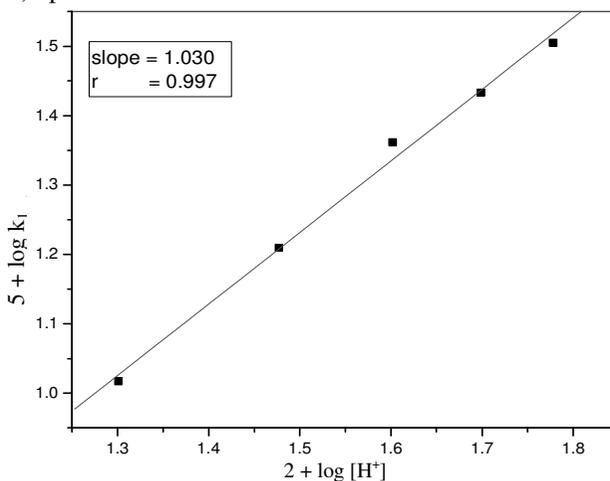


**Figure 1.** Variation of rate with benzaldehyde concentration.

*Effect of perchloric acid concentration*

The perchloric acid concentration was varied in the range of 0.2 to 0.6 mol dm<sup>-3</sup> and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table 1). The increase in [HClO<sub>4</sub>] in the oxidation reaction increases the

rate of the reaction and shows a direct first order dependence on  $[\text{HClO}_4]$ . A plot of  $\log k_1$  against  $\log [\text{H}^+]$  is linear. Change in ionic strength by the addition of  $\text{NaClO}_4$  has no effect on the rate constant. Under the acid concentrations used in the present investigations, the protonation of the aldehydes would be less significant. The possibility of the aldehydes getting protonated can be ruled out on the basis that aldehydes are extensively hydrated in an aqueous medium, and are present as equilibrium mixtures of the carbonyl and hydrated forms. The formation constants are thus not dependent on the acidity or alkalinity<sup>20</sup>. Hence, it would be justified to propose that in the range of acid concentrations used the oxidant IDC was converted to the protonated chromium(VI) species. Earlier reports have established the involvement of protonated Cr(VI) species in chromic acid oxidation reactions<sup>14</sup>.



**Figure 2.** Effect of variation of  $[\text{H}^+]$ .

#### *Effect of solvent composition*

The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 30% to 70%. The pseudo-first-order rate constants were estimated for the oxidation reactions of all of the substituted benzaldehydes, with IDC in the presence of perchloric acid at a constant ionic strength. The reaction rate increases markedly with the increase in the proportion of acetic acid in the medium (Table 2). When the acetic acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The observed effect is similar to those reported for the oxidation of benzaldehyde by quinolinium dichromate<sup>14</sup>.

The enhancement of the reaction rate with an increase in the amount of acetic acid generally may be attributed to two factors, *viz.*, (i) the increase in acidity occurring at constant  $[\text{H}^+]$  and (ii) the decrease in dielectric constant with an increase in the acetic acid content<sup>22</sup>. The magnitude of this effect could be analysed by suggesting that, for the equilibrium  $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ , a decrease in the dielectric constant of the medium would favour the dichromate form over the chromate form. If ion pairs were to be formed in this medium, it would be expected that they have a higher ion-pair association constant for the dichromate ion. Plots of  $\log k_1$  versus  $1/D$  were found to be linear, with positive slopes, which indicated that the reaction were of the ion-dipole type<sup>23</sup>.

**Table 2.** Effect of the solvent polarity on the rate of reaction at 303K  
 [BA] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [IDC] =  $1.2 \times 10^{-3}$  mol dm<sup>-3</sup>, [HClO<sub>4</sub>] =  $0.4$  mol dm<sup>-3</sup>.

Substrate	10 <sup>4</sup> k <sub>1</sub> <sup>a</sup> , s <sup>-1</sup> (AcOH : H <sub>2</sub> O (v/v), %)				Slope <sup>b</sup>	r <sup>b</sup>
	40-60	50-50	60-40	70-30		
<i>p</i> - OCH <sub>3</sub>	0.41	0.58	0.64	0.92	31.6	0.982
<i>p</i> - CH <sub>3</sub>	0.93	1.16	1.34	1.63	22.2	0.978
H	1.86	2.30	2.90	3.40	24.9	0.986
<i>p</i> - Cl	3.20	3.80	4.60	5.32	20.5	0.994
<i>p</i> -CN	11.20	12.40	13.80	15.28	12.8	0.997
<i>p</i> - NO <sub>2</sub>	13.50	15.00	18.00	20.88	18.2	0.997

<sup>a</sup> Estimated from pseudo-first-order reaction plots,

<sup>b</sup> These values were calculated from the plots drawn between log k<sub>1</sub> and 1/D.

### Mechanism and rate law

The sequence of reactions for the oxidation of benzaldehydes by IDC, in an acid medium is shown in Scheme1. In an acid medium, the oxidant IDC is converted to the protonated bimetallic chromium(VI) species (PIm). The protonated IDC would have the Cr(VI) existing mainly as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. The substrate (BA) was converted to hydrated form (HY). The reaction of the hydrated form (HY) of the substrate with the protonated IDC (PIm) resulted in the formation of the monochromate ester<sup>21</sup> which undergo decomposition in the rate determining step give the product.

Based on the mechanism shown in Scheme1, the rate law has been derived as follows:

$$-d[\text{IDC}] / dt = k_3 [\text{E}] = k_3 [\text{HY}] [\text{PIm}], \quad (2)$$

$$\text{Where, } [\text{PIm}] = K_1[\text{IDC}] [\text{H}^+], \text{ and } [\text{HY}] = K_2 [\text{BA}] [\text{H}_2\text{O}].$$

Substituting the values of [PIm] and [HY], the following equation was obtained:

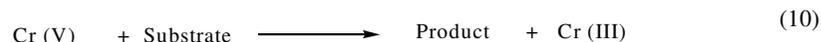
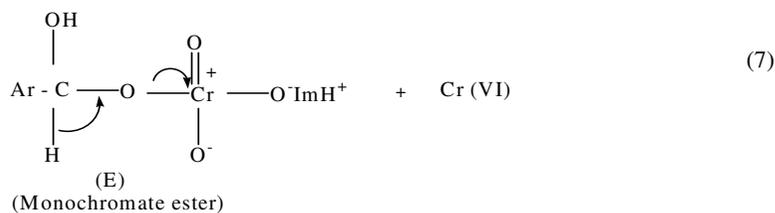
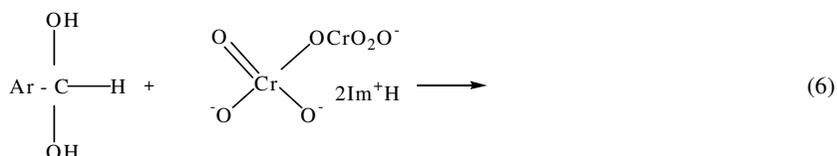
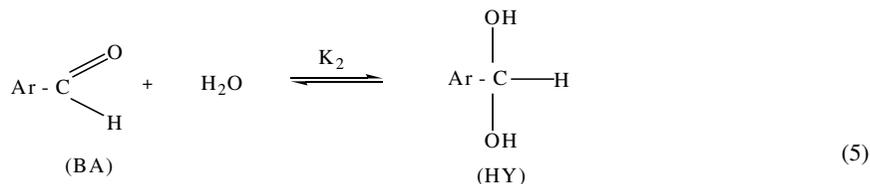
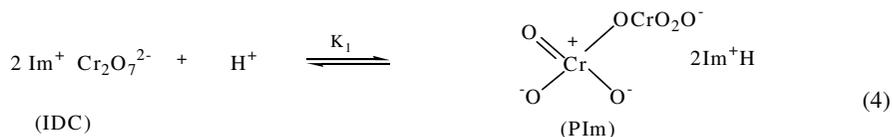
$$-d[\text{IDC}] / dt = K_1 K_2 k_3 [\text{BA}] [\text{IDC}] [\text{H}_2\text{O}] \quad (3)$$

From this expression, it is clear that the reaction exhibited first-order dependence with respect to the concentrations of each substrate, oxidant and acid. This rate law explains all the experimentally observed results.

### Oxidation of some *para*-substituted benzaldehydes with IDC

In order to study the effect of structure on reactivity, some *para*-substituted benzaldehydes were subjected to oxidation kinetics by IDC at four different temperatures *viz.*, 298, 303, 308 and 313 K in 50% - 50% (v/v) acetic acid – water medium in presence of perchloric acid. Substrate effect reveals that *para*-substituted benzaldehydes also first order dependence. The second order rate constants at four different temperatures with the activation parameters are given in the Table 3. It is interesting to note that the reactivity decreases in the order *p*-NO<sub>2</sub> > *p*-CN > *p*-Cl > *p*-H > *p*-CH<sub>3</sub> > *p*-OCH<sub>3</sub> for the substituents.

The Exner plot log k<sub>2</sub> (303 K) *versus* log k<sub>2</sub> (313 K) is linear (Figure 3; r = 0.996, SD = 0.031) and the isokinetic temperature β obtained from the slope is 413 K. This supports the arguments that all the reactions under this investigation follow a common mechanism<sup>24</sup>. The Hammett plot is also linear (r = 0.992, SD = 0.03) with ρ = +1.30 at 303K. According to Hammett<sup>25</sup> reaction with positive ρ values are accelerated by electron withdrawal from benzene ring, whereas those with negative ρ values are retarded by electron withdrawal from benzene ring. In this oxidation reactions, the electron withdrawing group increases the rate and the electron donating group decreases the rate. These observations supporting the positive ρ value obtained from the Hammett plot.



Scheme 1

**Table 3.** Second-order rate constants and activation parameters for the oxidation of benzaldehyde and some *para*-substituted benzaldehydes by IDC.

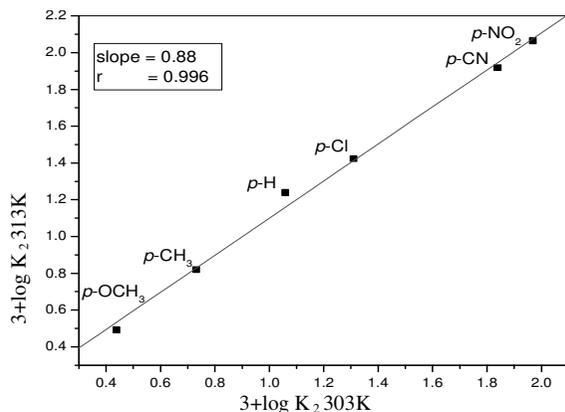
$$[\text{BA}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 0.4 \text{ mol dm}^{-3}$$

$$[\text{IDC}] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{AcOH} - \text{H}_2\text{O} = 50\% - 50\% (\text{v/v})$$

Substituents	$10^2 k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$				$E_a$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>
	298K	303K	308K	313K				
<i>p</i> -OCH <sub>3</sub>	0.23	0.29	0.38	0.55	44.1	42.10	154.46	88.9
<i>p</i> -CH <sub>3</sub>	0.40	0.58	0.72	0.84	38.0	35.47	171.36	87.4
H	0.80	1.15	1.50	1.98	45.7	43.15	140.13	85.6
<i>p</i> -Cl	1.47	1.90	2.60	3.00	38.1	27.65	186.16	84.1
<i>p</i> -CN	4.83	6.20	7.00	8.40	27.7	25.12	185.65	81.4
<i>p</i> -NO <sub>2</sub>	6.00	7.50	8.80	9.60	22.9	21.88	194.61	80.9



**Figure 3.** Exner plot between  $\log k_2$  (313K) versus  $\log k_2$  (303 K).

## Conclusions

The oxidation of benzaldehyde by IDC is an acid catalysed reaction and yields the corresponding benzoic acid as the product. The reaction is first order each in [Substrate], [Oxidant] and  $[H^+]$ . The stoichiometry was found to be 3 mol of aldehydes consuming 2 mol of IDC. The plots of  $\log k_1$  versus  $1/D$  were found to be linear, with positive slopes. The negative values of  $\Delta S^\ddagger$  provided support for the formation of a rigid activated complex.

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