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# Oxidation of Benzaldehydes by Quinolinium Dichromate-A Kinetic Study

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Oxidation of benzaldehydes (BZA) by quinolinium dichromate (QDC) in aqueous acetic acid is acid catalysed and is first order in (QDC) and also in (BZA). A cation dipole type of interaction between benzaldehyde and the oxidant is indicated. Electron-withdrawing substituent enhances the rate of oxidation while electron-donating group reduces the oxidation rate compared to the unsubstituted benzaldehyde. The rate data is correlated with $\sigma$ and $(\sigma^+-\sigma)$ according to Yukawa-Tsuno equation. The products identified are the corresponding benzoic acid and Cr(III) ion. Thermodynamic parameters are computed and a probable mechanism is proposed.

## INTRODUCTION

In recent years a variety of chromium(VI) complexes have been prepared and tested as effective oxidants[1–5]. Quinolium dichromate (QDC) is one of them. It has been first prepared and tested as oxidant by Balasubramanian[5]. But, so far no kinetic studies have been reported on its reactions as an oxidant. We report here our work on kinetics of oxidation of benzaldehyde and substituted benzaldehydes by this oxidant.

## RESULTS AND DISCUSSION

The reaction is first order with respect to [QDC] as evidenced by the linear plots of log $[QDC]_t$ against time at different initial concentrations of the oxidant under pseudo first order conditions and $k_{obs}$ values are nearly constant.

To study the effect of [benzaldehyde] on rate, the $k_{obs}$ values were determined (Table 1) at different concentrations of benzaldehyde, keeping all the other factors the same. The plots of log $k_{obs}$ versus log [benzaldehyde] are linear with nearly unit positive slopes with all the benzaldehydes studied. This observation shows that the reaction is first-order in [benzaldehyde].

Increase in the percentage (v/v) of acetic acid in the solvent mixture increases the rate (Table 2), suggesting that a medium of low dielectric constant favours the oxidation process. Correlation of log $k_{obs}$ with the reciprocal of the dielectric constant of the medium gives linear plots with all the benzaldehydes studied.

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This observation points to either an ion-ion or a cation-dipole type of interaction between the oxidant and the substrate. But, change in the ionic strength of the medium has only marginal effect on rate, ruling out the possibility of ion-ion type of interaction between the reactants. Hence, it is assumed to be a cation-dipole type interaction. The slopes of these plots are in the range of +25 to +50.0 for the different benzaldehydes, which indicates a reaction involving an ion-dipole type interaction[6].

TABLE 1
EFFECT OF [SUBSTRATE] ON $k_{obs}$ : BZA-QDC System. [QDC] = 0.002 mol. $dm^{-3}$; [$H_2SO_4$] = 1.0 mol. $dm^{-3}$; Aq.AcOH = 30% (v/v); temp. = 303 K

| Substrate | $10^5 \times k_{obs}$ $s^{-1}$ at [Substrate] mol. $dm^{-3}$ (C) | | | | Slope of log k *vs.* log C plot |
|---|---|---|---|---|---|
| | 0.025 | 0.05 | 0.075 | 0.10 | |
| BZA | 3.16 | 5.63 | 7.63 | 10.11 | 0.86 |
| *o*–ClBZA | 2.68 | 5.38 | 8.16 | 10.64 | 1.00 |
| *p*–ClBZA* | 16.54 | 32.48 | — | — | 0.98 |
| *m*–$NO_2$ BZA | 12.52 | 25.76 | 39.63 | — | 1.02 |
| *p*–$NO_2$ BZA** | 20.20 | 54.83 | — | — | 1.30 |
| *m*–$OCH_3$ BZA | 5.41 | 10.21 | 13.78 | 19.37 | 0.93 |
| *p*–$OCH_3$ BZA | 1.11 | 2.13 | 3.32 | 4.08 | 0.94 |

*Aq. AcOH = 70% (v/v) **Aq. AcOH = 40% (v/v)

TABLE 2
EFFECT OF SOLVENT ON $k_{obs}$ : BZA-QDC System. [Substrate] = 0.05 mol. $dm^{-3}$; [QDC] = 0.002 mol. $dm^{-3}$; [$H_2SO_4$] = 1.0 mol. $dm^{-3}$; temp = 303 K

| Substrate | $10^5 \times k_{obs}$ $S^{-1}$ at Aq. AcOH % (v/v) | | | | | | Slope of log k *vs.* 1/D plot |
|---|---|---|---|---|---|---|---|
| | 30% | 40% | 50% | 60% | 70% | 80% | |
| BZA | 5.63 | 7.17 | 11.63 | 14.96 | — | — | + 50.4 |
| *o*–Cl BZA | 5.38 | 7.32 | 10.83 | 19.28 | — | — | + 50.2 |
| *m*–Cl BZA | 8.62 | 11.69 | 17.80 | 29.08 | 78.49 | — | + 50.8 |
| *p*–Cl.BZA | — | — | — | 17.85 | 32.48 | 92.32 | + 34.3 |
| *m*–$NO_2$ BZA | 25.76 | 36.22 | 51.07 | 81.56 | 163.77 | — | + 40.5 |
| *p*–$NO_2$ BZA | — | 54.83 | 74.04 | 127.55 | 259.11 | — | + 43.0 |
| *m*–$OCH_3$ BZA | 10.21 | 11.77 | 16.87 | 18.97 | — | — | + 24.5 |
| *p*–$OCH_3$ BZA | 2.13 | 2.35 | 3.81 | 5.65 | 11.81 | — | + 40.0 |

The reaction is acid catalysed. Increases in [$H_2SO_4$] in the range 0.5 to 2.5 mol $dm^{-3}$ increases the oxidation rate (Table 3) and a plot of log $k_{obs}$ versus log $C_H$+ is linear with unit positive slope. For the calculation of $C_H$+, it is assumed that $H_2SO_4$ liberates only one proton in the range of [$H_2SO_4$] used. According to Zücker Hammett Criterion[7] this unit positive slope suggests the involvement of water molecule in rate-determining step. This is further confirmed by Bunnett's hypothesis[8] and Bunnett-Olsen's LFER[9].

TABLE 3
EFFECT OF $[H_2SO_4]$ on $k_{obs}$ : BZA-QDC system [Substrate] = 0.05 mol. $dm^{-3}$; [QDC] = 0.002 mol. $dm^{-3}$; Aq.AcOH = 30% (v/v); temp = 303 K

| Substrate | $10^5 \times k_{obs}$ $S^{-1}$ at $[H_2SO_4]$ mol. $dm^{-3}$ | | | | | ω | ϕ |
|---|---|---|---|---|---|---|---|
| | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | | |
| BZA | 2.73 | 5.63 | 9.39 | 10.97 | 13.80 | 11.40 | 1.02 |
| *o*–Cl BZA | 2.70 | 5.38 | 8.18 | 11.42 | 12.30 | 9.68 | 0.93 |
| *m*–Cl BZA | 4.99 | 8.62 | — | 15.93 | 29.48 | 6.82 | 1.27 |
| *p*–Cl BZA* | 15.38 | 32.48 | — | 91.05 | 275.71 | 4.00 | 0.52 |
| *m*–$NO_2$ BZA | 11.79 | 25.76 | — | 60.37 | 79.43 | 8.91 | 0.87 |
| *p*–$NO_2$ BZA** | 23.62 | 54.83 | — | 117.51 | 156.68 | 8.91 | 0.87 |
| *m*–$OCH_3$ BZA | 4.73 | 10.21 | — | 26.61 | 45.21 | 3.94 | 0.48 |
| *p*–$OCH_3$ BZA | 1.68 | 2.13 | — | 5.05 | 7.74 | 9.60 | 0.65 |

*Aq.AcOH = 70% (v/v) **Aq.AcOH = 40% (v/v)

According to Bunnett's hypothesis, in any acid catalysed reaction $\log k_{obs} + H_o$ against $\log a_{H_2O}$ ($H_o$ is Hammett's acidity function an $a_{H_2O}$ is activity of water) would be linear (slope ω). The sign and magnitude of ω indicate the nature of participation of water molecule in the rate determining step of the reaction. In the present case the above plot is linear and ω is $> +3.3$ with all the benzaldehydes studied, suggesting that water acts as a proton transfer agent in the slow step. Further, Bunnett-Olsen's plot of $\log k_{obs} + H_o$ against $\log C_{acid} + H_o$ is also linear with a slope $(\phi) \geq +0.48$ in all the cases. According to Bunnett-Olsen's criterion[9] the slope 'ϕ' which is $> 0.58$ suggests that the water molecule acts as a proton transfer agent in the rate determining step. In the present case with an exception to *p*-Cl and *m*-$OCH_3$ benzaldehydes, with all the other benzaldehydes studied, we observed that $\phi > 0.58$. So, it is concluded that water acts as a proton transfer agent in the rate determining step.

Based on these observations, the rate law for the oxidation process can be written as:

$$-\frac{d[QDC]}{dt} = K_{II}\,[QDC]\,[BZA]\,[H^+] \qquad (1)$$

The reaction system failed to induce the polymerisation of added acrylonitrile suggesting the absence of free radical intermediates in the oxidation process. Under similar experimental conditions $k_{D_2O}/k_{H_2O}$ is found to be 1.2 as expected for any acid catalysed reaction.

Table–4 shows the effect of substituent on the rate of oxidation of benzaldehyde. Under similar experimental conditions an electron withdrawing group on benzene ring enhances the rate of oxidation, while electron donating group reduces the rate of oxidation compared to that of the unsubstituted one. Among the benzaldehydes used for the oxidation study, the order of reactivity is: $p-NO_2 > m-NO_2 > m-Cl > o-Cl > m-OCH_3 > p-Cl > H > p-OCH_3$. The correlation of $\log k_{obs}$ with Hammett's substituent constant[10] σ gives a linear plot with

TABLE 4
ACTIVATION PARAMETERS FOR BZA-QDC SYSTEM
[Substrate] = 0.05 mol. $dm^{-3}$; $H_2SO_4$ = 1.0 mol. $dm^{-3}$; Aq. AcOH = 60% (v/v);
[QDC] = 0.002 mol. $dm^{-3}$; temp = 303 K

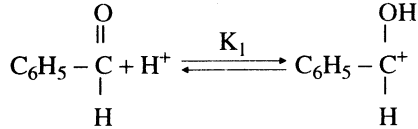
| Substrate | $k \times 10^3$ $dm^6\ mol^{-2}\ s^{-1}$ | $\Delta H^{\neq}$ kJ $mol^{-1}$ | $-\Delta S^{\neq}$ $JK^{-1}\ mol^{-1}$ | $\Delta G^{\neq}$ kJ $mol^{-1}$ |
|---|---|---|---|---|
| BZA | 2.99 | 67.84 | 69 | 88.75 |
| *o*–Cl BZA | 3.86 | 36.65 | 170 | 88.16 |
| *m*–Cl BZA | 5.82 | 43.85 | 143 | 87.18 |
| *p*–Cl BZA | 3.57 | 53.28 | 116 | 88.43 |
| *m*–$NO_2$ BZA | 16.31 | 32.51 | 172 | 84.63 |
| *p*–$NO_2$ BZA | 25.51 | 34.63 | 153 | 80.99 |
| *m*–$OCH_3$ BZA | 3.79 | 38.65 | 164 | 88.34 |
| *p*–$OCH_3$ BZA | 1.13 | 46.91 | 146 | 91.15 |

a positive slope of 1.20 (r = 0.97). Correlation of rate data with $\sigma$ is also satisfactory with r = 0.98, suggesting a resonance interaction between the reaction centre and the substituents. The kinetic data also have been analysed using Yukawa-Tsuno equation[11].

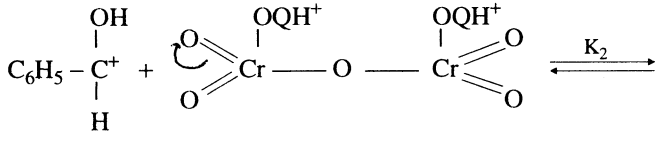
$$\log k = \log k_0 + \rho\,[\sigma + r\,(\sigma^+ - \sigma)] \qquad (2)$$

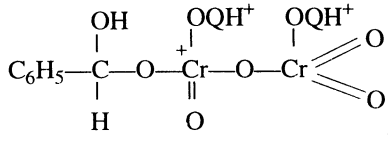
In this relation the value of $(\sigma^+ - \sigma)$ would provide a scale of enhanced resonance effects and *r* is the proportionality constant which gives the contribution of this enhanced resonance effect. Usually *r* value lies between zero and unity. In the present case when multiple correlation of log $k_{obs}$ with $\sigma$ and $(\sigma^+ - \sigma)$ is done a satisfactory correlation is observed with a correlation coefficient of 0.99. The value obtained is 1.0 and $r = 0.32$. This positive *r* value shows that the transition state structure is stabilized by resonance.

Keeping these observations in view the following probable mechanism is proposed:



(3)





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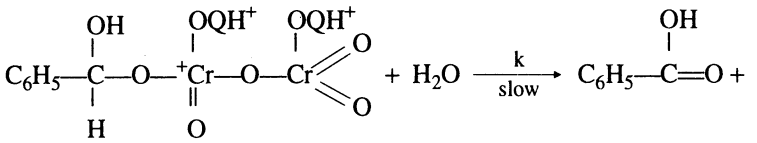

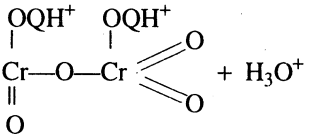

(5)

$$Cr(IV)—O—Cr(VI) \xrightarrow{H_2O} Cr(V)—O—Cr(V) \qquad (6)$$

$$Cr(V)—O—Cr(V) + 2\,C_6H_5CHO \longrightarrow 2\,C_6H_5\overset{\overset{O}{\|}}{C}—OH + Cr(III)—O—Cr(III) \qquad (7)$$

The reaction involoves interaction between protonated benzaldehyde and QDC forming an ester, in a fast pre-equilibrium process, which then decomposes in a slow step forming benzoic acid. The product from the oxidant species [Cr(IV)–O–Cr(VI)] undergoes fast intramolecular electron transfer forming Cr(V)–O–Cr(V) and in turn oxidises two more moles of benzaldehyde ultimately forming Cr(III) which has been indentified by a spot test[12]. Such type of fast electron transfer between Cr(IV) and Cr(VI) to give Cr(V) has been reported earlier[13]. In addition to the Bunnett's criterion and Bunnett Olsen's LFER, the positive reaction constant ρ also supports the loss of aldehydic hydrogen atom as a proton in the slow step. This proton transfer is more favourable in the case of benzaldehydes with electron withdrawing groups on the benzene ring. The rate equation derived from this mechanism is

$$-\frac{d[QDC]}{dt} = k_{II}\,[BZA]\,[QDC]\,[H^+] \qquad (8)$$

$$[k_{II} = K_1\,K_2\,k]$$

The reactions were studied at different temperatures in the range 20°–45°C and the thermodynamic parameters enthalpy, entropy and free energy of activation $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ computed are given in Table–4. The entropy values are all negative and high, suggesting that the transition state is more rigid and extensively solvated than the reactants. The plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ is linear ($r = 0.97$), suggesting that all the benzaldehydes studied follow a similar mechanism. The isokinetic temperature obtained from the slope of this plot is 340 K. The linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ may not be due to compensation of errors in these factors, because there are large variations in these factors.

According to Exner's criterion[14], log $k_{obs}$ at 313 K and log $k_{obs}$ at 293 K are also linearly correlated with $r = 0.98$, confirming the operation, of a similar mechanism with all the benzaldehydes studied. The $\Delta G^{\neq}$ values computed vary

linearly with substituent constant $\sigma^+$ with a correlation coefficient of $r = 0.93$. This is in accordance with the relation[15]

$$\Delta G^{\neq} = -2.303\ RT\ \rho\sigma^+ \quad (9)$$

which shows the substituent effect on free energy of activation.

## EXPERIMENTAL

Benzaldehyde (BDH) was distilled before use. *p*–$NO_2$ and *m*–$OCH_3$ benzaldehydes (E-Merck), *m*–$NO_2$ benzaldehyde (Fluka AG), *p*–Cl benzaldehyde and *o*–Cl benzaldehyde (Riedel) were used as such. The oxidant QDC was prepared following reported procedure[5]. $D_2O$ (Sigma Chemical Company) was used as such. The kinetic studies were made in aqueous acetic acid (30% v/v) medium at 303 K. The reaction mixture consisted of 0.002 mol $dm^{-3}$ QDC, 0.05 mol $dm^{-3}$ benzaldehyde and 1.0 mol $dm^{-3}$ sulphuric acid. The temperature was maintained constant (± 0.2 °C).

The reaction was followed by estimating the concentration of unreacted QDC iodometrically at regular time intervals. From the slopes of the plots of log $[QDC]_t$ against time, the pseudo first-order rate constants, $k_{obs}$, were evaluated, which were reproducible within ± 5%. The stoichiometric studies revealed that 3 moles of benzaldehyde get oxidised by each mole of QDC. The final product from the oxidant is Cr(III), which has been identified by spot test with diphenyl carbazide[12]. After the completion of the reaction, the reaction mixture was extracted with ether and the ether extract was evaporated. The solid separated was identified to be the corresponding carboxylic acid. Benzoic acid (m.p. 120°C, lit. value 121.5°C) *m*–$NO_2$ benzoic acid (m.p. 141°C, lit. value 141°C), *p*–$OCH_3$ benzoic acid (m.p.185 °C, lit. value 184°C), *m*–$OCH_3$ benzoic acid (m.p. 109°C, lit. value 110°C) were obtained from the corresponding benzaldehydes. These were also identified by preparing the corresponding iso-thiuronium salts[16].

The regression analysis was carried on a PCL personal Computer.

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