



Oxidation of Some Aliphatic Aldehydes by Quinolinium Dichromate: A Kinetic and Mechanistic Study

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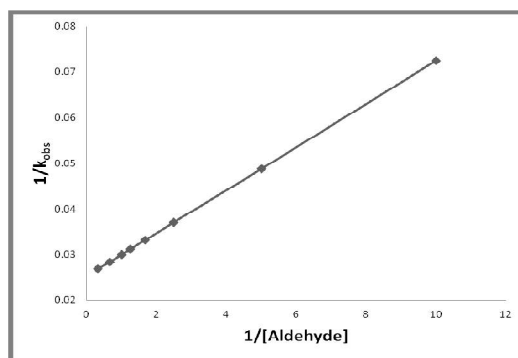
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Accepted on 1st May, 2018

ABSTRACT

The Oxidation of six aliphatic aldehydes by Quinolinium dichromate (QDC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order each in QDC. A Michaelis-Menten type of kinetics is observed with respect to the aldehydes. The reaction is catalysed by hydrogen ions, the hydrogen-ion dependence has the form $k_{obs} = a + b[H^+]$. The oxidation of deuteriated acetaldehyde, MeCDO, exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.78$ at 298 K). The oxidation of acetaldehyde has been studied in nineteen different organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's σ^* values, reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested.

Graphical Abstract



Oxidation of Aldehyde by QDC: A double reciprocal plot

Keywords: Aldehydes, Correlation Analysis, Halochromate, Kinetics, Mechanism, Oxidation.

INTRODUCTION

Salts of Cr(VI) have long been used as oxidizing reagents in synthetic organic chemistry. However, these salts are drastic and non-selective oxidants in nature. Further, they are insoluble in most of the organic solvents also. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents [1-4]. One such compound is Quinolinium dichromate (QDC) [5] used for the oxidation of alcohols to carbonyl compounds. It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. We have been interested in kinetic and mechanistic aspects of oxidation by complexed Cr(VI) species and several reports, by halochromates have already been reported [6-10]. Therefore, in continuation of our earlier work, we report here the kinetics and mechanism of oxidation of nine aliphatic primary alcohols by QDC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed.

The main aims of the present investigation are to (i) determine kinetic parameters and to evaluate the rate laws, (ii) to study the correlation analysis of effect of structure on Rate (iii) and to postulate a suitable mechanism for the oxidation process.

MATERIALS AND METHODS

QDC was prepared by the reported method [5] and its purity checked by an iodometric determinations. Solutions of formaldehyde were prepared by heating para-formaldehyde and passing its vapours in DMSO. The amount of HCHO in DMSO was determined by chromotropic acid method [11]. Other aldehydes were commercial products and were used as such. p-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. Deuteriated acetaldehyde (MeCDO) was obtained from Sigma Chemicals. Solvents were purified by their usual methods [12].

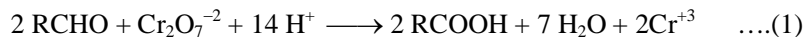
Product analysis: The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1mol) and QDC (1.88 g, 0.01mol) were dissolved in DMSO (100 mL) and the reaction mixture was allowed to stand for *ca.* \approx 24 h to ensure completion of the reaction. It was then rendered alkaline with NaOH, filtered and the filtrate was reduced to dryness under pressure. The residue was acidified with perchloric acid and extracted with diethyl ether (5%, 50 mL). The ether extract was dried (MgSO₄) and treated with 10 mL of thionyl chloride. The solvent was allowed to evaporate. Dry methanol (7 mL) was added and the HCl formed was removed in a current of dry air. The residue was dissolved in diethyl ether (200 mL) and the ester content was determined colorimetrically as Fe (III) hydroxamate by the procedure of Hall and Schaefer [13]. Several determinations indicated a 1:1 stoichiometry. The oxidation state of chromium in a completely reduced reaction mixture, determined by iodometric titrations was 3.95 ± 0.10 .

Kinetic Measurements: Pseudo-first-order conditions were attained by keeping an excess ($\times 15$ or greater) of the [aldehyde] over [QDC]. The solvent was DMSO, unless mentioned otherwise. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reactions were carried out at constant temperature (± 0.1 K) and were followed up to 80% of the extent of reaction, by monitoring the decrease in [QDC] at 352 nm. The pseudo-first-order rate constant, k_{obs} , was computed from the linear least-squares plot of $\log [\text{QDC}]$ versus time. Duplicate runs showed that the rate constants were reproducible to within $\pm 3\%$. The second order rate constant, k_2 , was calculated from the relation: $k_2 = k_{\text{obs}}/[\text{aldehyde}]$.

RESULTS AND DISCUSSION

The rate and other experimental data were obtained for all the aldehydes. Since the results are similar, only representative data are reproduced here.

Stoichiometry: The oxidation of aliphatic aldehydes by QDC leads to the formation of corresponding carboxylic acids. The overall reaction may be written as:

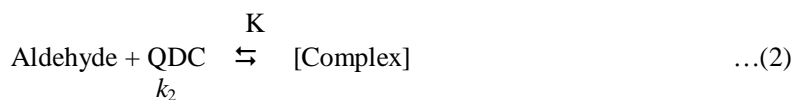


Rate-laws: The reactions are of first order with respect to QDC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of QDC. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1). The figure 1 depicts a typical kinetic run. A plot of $1/k_{\text{obs}}$ against $1/[\text{aldehyde}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate (figure 2). Thus, Michaelis-Menten type kinetics is observed with respect to the aldehydes. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

Table 1. Rate constants for the oxidation of acetaldehyde by QDC at 298 K

| $10^3 [\text{QDC}]$ mol dm^{-3} | $[\text{Aldehyde}]$ mol dm^{-3} | $10^4 k_{\text{obs}}$ s^{-1} |
|---|---|--|
| 1.00 | 0.10 | 13.8 |
| 1.00 | 0.20 | 20.5 |
| 1.00 | 0.40 | 27.0 |
| 1.00 | 0.60 | 30.2 |
| 1.00 | 0.80 | 32.1 |
| 1.00 | 1.00 | 33.4 |
| 1.00 | 1.50 | 35.2 |
| 1.00 | 3.00 | 37.3 |
| 2.00 | 0.20 | 22.5 |
| 4.00 | 0.20 | 21.6 |
| 6.00 | 0.20 | 23.4 |
| 8.00 | 0.20 | 19.8 |
| 1.00 | 0.40 | 28.8* |

* contained 0.001 M acrylonitrile



$$\text{Rate} = k_2 K [\text{Aldehyde}] [\text{QDC}] / (1 + K [\text{Aldehyde}]) \quad \dots(4)$$

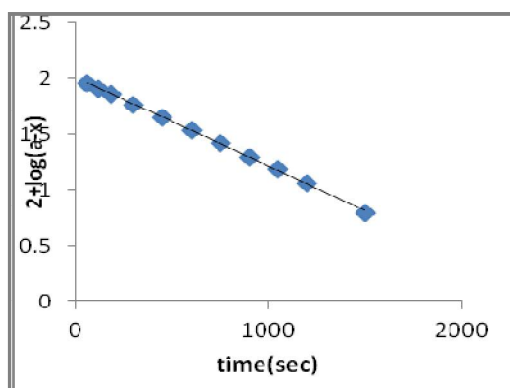


Figure 1. Oxidation of Acetaldehyde by QDC:
A typical Kinetic Run

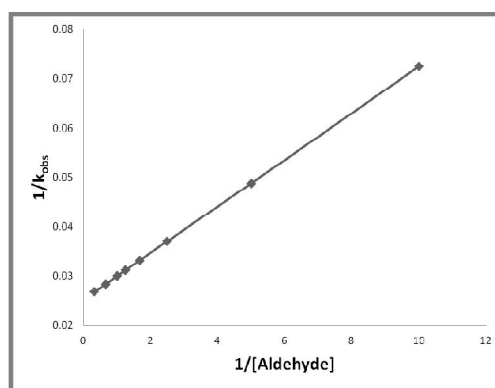


Figure 2. Oxidation of Aldehyde by QDC:
A double reciprocal plot

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The

thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 2 and 3).

Induced Polymerization of Acrylonitrile/test for free radicals: The oxidation of aldehydes, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that an one-electron oxidation, giving rise to free radicals, is unlikely in the present reaction (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2, 6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Table 2. Rate constants and activation parameters of the oxidation of aliphatic aldehydes – QDC complexes.

| Aldehyde | $10^4 k_2 / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ | | | | ΔH^* (kJ mol ⁻¹) | $-\Delta S^*$ (J mol ⁻¹ K ⁻¹) | ΔG^* (kJ mol ⁻¹) |
|-------------------|--|-------|-------|-------|---|---|---|
| | 288 K | 298 K | 308 K | 318 K | | | |
| H | 1.53 | 3.78 | 8.82 | 18.0 | 60.3±0.7 | 109±2 | 92.6±0.6 |
| Me | 18.0 | 39.6 | 82.8 | 171 | 54.5±0.3 | 109±1 | 86.7±0.2 |
| Et | 29.7 | 63.0 | 130 | 261 | 52.6±0.3 | 111±1 | 85.5±0.2 |
| Pr | 31.5 | 68.4 | 135 | 279 | 52.4±0.6 | 111±2 | 85.4±0.5 |
| Pr ⁱ | 45.9 | 98.1 | 198 | 387 | 51.5±0.1 | 111±1 | 84.5±0.1 |
| ClCH ₂ | 0.099 | 0.261 | 0.63 | 1.53 | 66.7±0.5 | 109±2 | 99.2±0.4 |
| MeCDO | 2.98 | 6.88 | 15.3 | 33.3 | 58.7±0.4 | 109±1 | 91.0±0.3 |
| k_H/k_D | 6.04 | 5.75 | 5.41 | 5.13 | | | |

Table 3. Formation constants and thermodynamic parameters of the oxidation of aliphatic aldehydes – QDC complexes.

| Aldehyde | $K (\text{dm}^3 \text{mol}^{-1})$ | | | | $-\Delta H^*$ (kJ mol ⁻¹) | $-\Delta S^*$ (J mol ⁻¹ K ⁻¹) | $-\Delta G^*$ (kJ mol ⁻¹) |
|-------------------|-----------------------------------|-------|-------|-------|--|---|--|
| | 288 K | 298 K | 308 K | 318 K | | | |
| H | 5.94 | 5.25 | 4.53 | 3.78 | 13.9±0.6 | 25±2 | 6.56±0.5 |
| Me | 6.03 | 5.35 | 4.62 | 3.90 | 13.5±0.5 | 24±2 | 6.61±0.4 |
| Et | 5.85 | 5.16 | 4.43 | 3.72 | 14.0±0.5 | 25±2 | 6.52±0.4 |
| Pr | 5.76 | 5.06 | 4.30 | 3.63 | 14.2±0.5 | 27±2 | 6.47±0.4 |
| Pr ⁱ | 6.06 | 5.35 | 4.65 | 3.90 | 13.6±0.6 | 24±2 | 6.61±0.4 |
| ClCH ₂ | 5.58 | 4.82 | 4.16 | 3.45 | 14.6±0.5 | 28±2 | 6.37±0.4 |
| MeCDO | 61.5 | 5.45 | 4.72 | 3.96 | 13.6±0.6 | 24±2 | 6.65±0.05 |

Kinetic isotope effect: To ascertain the importance of the cleavage of the aldehydic C–H bond in the rate-determining step, the oxidation of deuteriated acetaldehyde (MeCDO) was studied. The oxidation of deuteriated acetaldehyde exhibited a substantial primary kinetic isotope effect (Table 2).

Effect of acidity: The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen-ion dependence has the following form $k_{\text{obs}} = a + b[\text{H}^+]$. The values of a and b , for acetaldehyde, are $4.05 \pm 0.12 \times 10^{-4} \text{ s}^{-1}$ and $7.46 \pm 0.21 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($R^2 = 0.99708$).

Table 4. Dependence of the reaction rate on hydrogen-ion concentration

| [QDC] = 0.001 mol dm ⁻³ | | [Aldehyde] = 1.0 mol dm ⁻³ | | | Temp. = 318 K | |
|---|------|---------------------------------------|------|------|---------------|------|
| [H ⁺]/mol dm ⁻³ | 0.10 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| 10 ⁴ /k _{obs} s ⁻¹ | 17.1 | 18.9 | 24.3 | 28.8 | 33.3 | 39.6 |

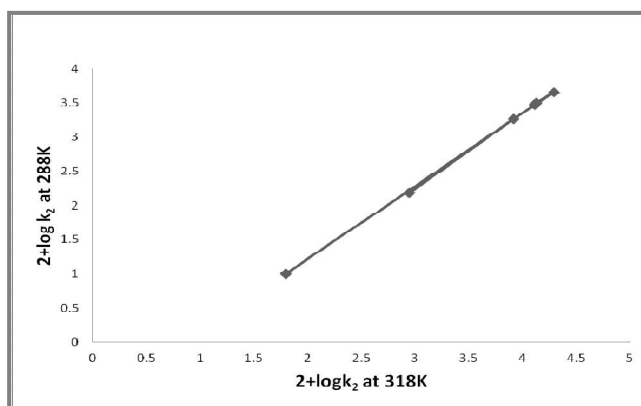
$$\text{Rate} = k_2 [\text{QDC}] [\text{Aldehyde}] + k_3 [\text{QDC}] [\text{Aldehyde}] [\text{TsOH}] \quad \dots(5)$$

Effect of solvents: The oxidation of acetaldehyde was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of QDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values k₂ are recorded in table 5.

Table 5. Effect of solvents on the oxidation of acetaldehyde-QDC complex at 298 K.

| Solvents | K (dm ⁻³ mol ⁻¹) | 10 ⁴ k _{obs} (s ⁻¹) | Solvents | K (dm ⁻³ mol ⁻¹) | 10 ⁴ k _{obs} (s ⁻¹) |
|--------------------|---|---|---------------------|---|---|
| Chloroform | 5.66 | 12.0 | Toluene | 5.04 | 3.47 |
| 1,2-Dichloroethane | 5.55 | 14.8 | Acetophenone | 5.88 | 16.6 |
| Dichloromethane | 6.10 | 11.5 | THF | 4.95 | 6.46 |
| DMSO | 5.35 | 39.6 | t-Butylalcohol | 5.60 | 4.57 |
| Acetone | 6.03 | 12.9 | 1,4-Dioxane | 5.73 | 5.62 |
| DMF | 5.45 | 18.2 | 1,2-Dimethoxyethane | 5.50 | 3.31 |
| Butanone | 5.90 | 9.77 | CS ₂ | 6.11 | 1.86 |
| Nitrobenzene | 5.85 | 17.4 | Acetic Acid | 5.77 | 2.82 |
| Benzene | 5.70 | 4.27 | Ethyl Acetate | 5.58 | 5.25 |
| Cyclohexane | 6.21 | 0.44 | | | |

There is a fair correlation between the activation enthalpies and entropies of the oxidation of aldehydes (R² = 0.9809), indicating the operation of a compensation effect [14]. A correlation between the calculated values of enthalpies and entropies is often vitiated by the experimental errors associated with them. The reaction, however, exhibited an excellent isokinetic relationship, as determined by Exner's method [15]. An Exner's plot between log k₂ at 288 K and at 318 K was linear (R² = 0.9999) (figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 1513±133 K. The linear isokinetic correlation implies that all the aldehydes are oxidized by the same mechanism and the change in the rate of oxidation is governed by changes in both the enthalpy and entropy of the activation.

**Figure 3.** Exner's Isokinetic Relationship in the oxidation of Aldehydes by QDC

Solvent effect: The rate constants, k_2 , in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (6) of Kamlet *et al* [16].

$$\log k_2 = A_0 + \rho\pi^* + b\beta + a\alpha \quad \dots(6)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α . The results of correlation analyses in terms of (6), a biparametric equation involving π^* and β , and separately with π^* and β are given below as equation (7) - (10).

$$\log k_2 = -3.74 + 1.64 (\pm 0.18) \pi^* + 0.15 (\pm 0.15) \beta + 0.05 (\pm 0.14) \alpha \quad \dots(7)$$

$$R^2 = 0.8748; \text{ sd} = 0.17; \text{ n} = 18; \psi = 0.37$$

$$\log k_2 = -3.73 + 1.66 (\pm 0.17) \pi^* + 0.14 (\pm 0.14) \beta \quad \dots(8)$$

$$R^2 = 0.8735; \text{ sd} = 0.16; \text{ n} = 18; \psi = 0.38$$

$$\log k_2 = -3.75 + 1.70 (\pm 0.17) \pi^* \quad \dots(9)$$

$$R^2 = 0.8656; \text{ sd} = 0.16; \text{ n} = 18; \psi = 0.38$$

$$\log k_2 = -3.31 + 0.43 (\pm 0.36) \beta \quad \dots(10)$$

$$R^2 = 0.0841; \text{ sd} = 0.43; \text{ n} = 18; \psi = 0.98$$

Here n is the number of data points and ψ is the Exner's statistical parameter [17].

Kamlet's [16] triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion [17] the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 86% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analyzed in terms of Swain's equation [18] of cation- and anion-solvating concept of the solvents also as equation (11).

$$\log k_2 = aA + bB + C \quad \dots(11)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A + B)$ is postulated to represent the solvent polarity. The rates in different solvents were analyzed in terms of equation (8), separately with A and B and with $(A + B)$.

$$\log k_2 = 0.72 (\pm 0.04) A + 1.68 (\pm 0.03) B - 4.46 \quad \dots(12)$$

$$R^2 = 0.9941; \text{ sd} = 0.04; \text{ n} = 19; \psi = 0.08$$

$$\log k_2 = 0.49 (\pm 0.55) A - 3.31 \quad \dots(13)$$

$$R^2 = 0.0434; \text{ sd} = 0.45; \text{ n} = 19; \psi = 1.00$$

$$\log k_2 = 1.62 (\pm 0.13) B - 4.22 \quad \dots(14)$$

$$R^2 = 0.8988; \text{ sd} = 0.14; \text{ n} = 19; \psi = 0.33$$

$$\log k_2 = 1.36 \pm 0.12 (A + B) - 4.43 \quad \dots(15)$$

$$R^2 = 0.8753; \text{ sd} = 0.16; \text{ n} = 19; \psi = 0.36$$

The rates of oxidation of acetaldehyde in different solvents showed an excellent correlation in Swain's equation [cf. (12)] with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for *ca.* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 87% of the data. In view of the fact that solvent polarity is able to account for *ca.* 87% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($R^2 = 0.5286$; $sd = 0.31$; $\psi = 0.71$).

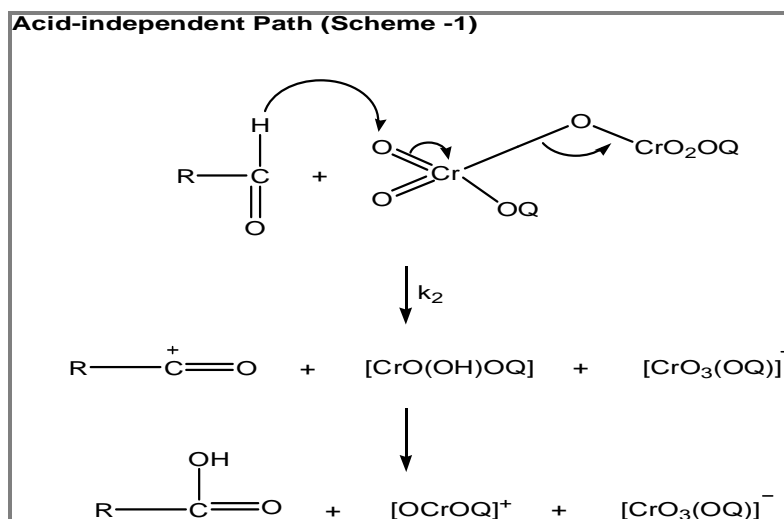
Correlation analysis of reactivity: The rates of the oxidation of six aldehydes show an excellent correlation with Taft's σ^* substituent constants [19], the reaction constant being negative (Table 6). The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step.

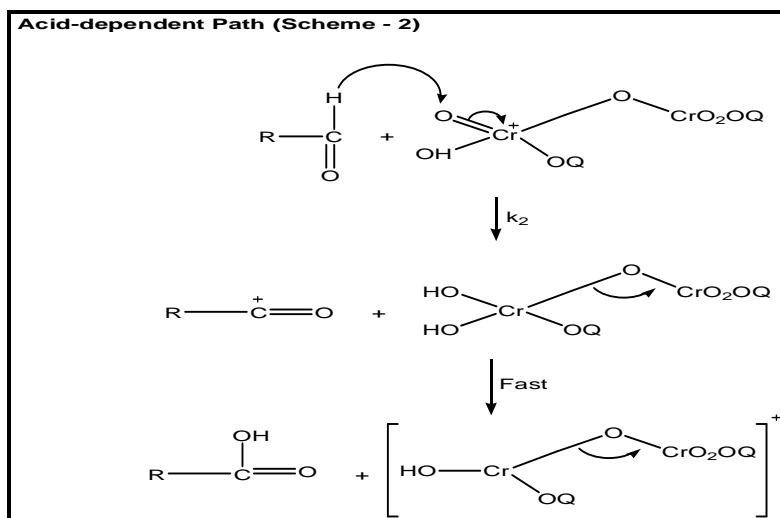
Table 6. Temperature dependence of the reaction constant

| Temp. in K | $-\rho^*$ | r^2 | sd | ψ |
|------------|-----------|--------|-------|--------|
| 288 | 2.15±0.01 | 0.9999 | 0.007 | 0.01 |
| 298 | 2.07±0.01 | 0.9998 | 0.002 | 0.02 |
| 308 | 2.00±0.01 | 0.9998 | 0.011 | 0.02 |
| 318 | 1.91±0.02 | 0.9997 | 0.018 | 0.02 |

Mechanism: In aqueous solutions most aliphatic aldehydes exist predominantly in the hydrate form [20] and in many oxidations, in aqueous solutions, it has been postulated that the hydrate is the reactive species. However, owing to the non-aqueous nature of the solvent in the present reaction, only the free carbonyl form can be the reactive species. The presence of a substantial primary kinetic isotope effect ($k_H/k_D = 5.75$ at 298 K), confirms that the aldehydic C-H bond is cleaved in the rate-determining step. The large negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, transfer of a hydride ion from the aldehyde to the oxidant is suggested. The hydride ion transfer mechanism is also supported by major role of cation-solvating power of the solvents.

High values of activation indicate that in the rate determining step bond breaking is more important in transition state. Large negative entropy of activation supports a transition state formed from two independent molecules.





CONCLUSIONS

The reaction is proposed to proceed through a hydride-ion transfer from aldehyde to the oxidant. The hydride ion transfer mechanism is also supported by major role of cation-solvating power of the solvents. Both deprotonated and protonated forms of QDC are the reactive oxidizing species. An aldehydic C–H bond is cleaved in the rate-determining step.

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