



OXIDATION OF SOME ALIPHATIC ALDEHYDES BY QUINOLINIUM CHLOROCHROMATE: A KINETIC AND MECHANISTIC STUDY

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The oxidation of six aliphatic aldehydes by quinolinium chlorochromate (QCC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order in QCC. 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: $k_{\text{obs}}=a + b[\text{H}^+]$. The oxidation of deuterated acetaldehyde, MeCDO, exhibited a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}=5.78$ 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.

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and passing its vapours in DMSO. The amount of HCHO in DMSO was determined by chromotropic acid method⁸. Other aldehydes were commercial products and were used as such. p-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. Deuterated acetaldehyde (MeCDO) was obtained from Sigma Chemicals. Solvents were purified by their usual methods.⁹

Introduction

Various halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry.¹ Quinolinium chlorochromate (QCC) is one such compound used for the oxidation of compounds of industrial importance.² Oxidation of substituted benzaldehydes with various oxidants is an intensively studied area as well.³ We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several reports on halochromates have already been reported from our laboratory.⁴⁻⁶ There seems to be only a few reports on the oxidation aspects of QCC are available in literature.⁷ In continuation of our earlier work, we report here the kinetics and mechanism of oxidation of six aliphatic aldehydes by QCC 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 and (iii) to postulate a suitable mechanism for the oxidation process.

Experimental Section

Materials

QCC was prepared by the reported method² and its purity checked by an iodometric determinations. Solutions of formaldehyde were prepared by heating para-formaldehyde

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1mol) and QCC (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 (MgSO_4) 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) hydroxymate by the procedure of Hall and Schaefer.¹⁰ 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 ± 0.1 .

Kinetic Measurements

Pseudo-first-order conditions were attained by keeping an excess ($\times 15$ or greater) of the [aldehyde] over [QCC]. 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

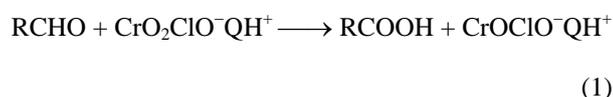
monitoring the decrease in [QCC] at 352 nm. The pseudo-first-order rate constant, k_{obs} , was computed from the linear least-squares plot of $\log [\text{QCC}]$ versus time. Duplicate runs showed that the rate constants were reproducible to within $\pm 3\%$. The second order rate constant, k_2 , was calculated from the relation: $k_2 = k_{\text{obs}}/[\text{aldehyde}]$.

Results

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 QCC leads to the formation of corresponding carboxylic acids. The overall reaction may therefore, be written as:



QCC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both pyridinium chlorochromate (PCC)¹¹ and pyridinium fluorochromate (PFC)¹² act as two electron oxidants and are reduced to chromium (IV) species, determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

Rate-laws

The reactions are of first order with respect to QCC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of QCC. The reaction rate increases with increase in the concentration of the aldehydes but not linearly (Table 1).

Table 1. Rate constants for the oxidation of acetaldehyde by QCC at 288 K

$10^3 [\text{QCC}]$ mol dm^{-3}	$[\text{MeCHO}]$ mol dm^{-3}	$[\text{TsOH}]$ mol dm^{-3}	$10^4 k_{\text{obs}}$ s^{-1}
1.00	0.10	0.00	7.79
1.00	0.20	0.00	11.3
1.00	0.40	0.00	14.3
1.00	0.60	0.00	16.2
1.00	0.80	0.00	17.1
1.00	1.00	0.00	17.8
1.00	1.50	0.00	18.6
1.00	3.00	0.00	19.6
2.00	0.40	0.00	15.5
4.00	0.40	0.00	14.6
6.00	0.40	0.00	15.0
8.00	0.40	0.00	14.4
1.00	0.20	0.00	12.6

* contained $0.001 \text{ mol dm}^{-3}$ acrylonitrile

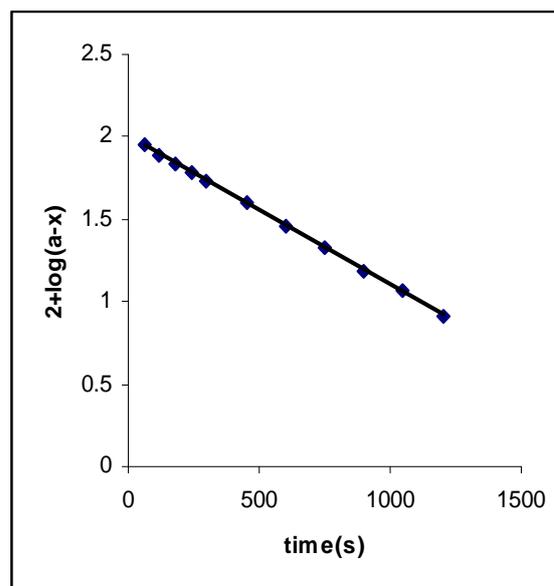
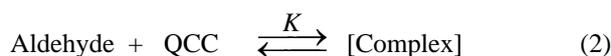


Figure 1. Oxidation of Acetaldehyde by QCC: A typical Kinetic Run

The Fig 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 (Fig. 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).



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 3 and 4).

$$\text{Rate} = \frac{k_2 K [\text{Aldehyde}] [\text{QCC}]}{1 + K [\text{Aldehyde}]} \quad (4)$$

Induced polymerization of acrylonitrile/test for free radicals

The oxidation of aldehydes, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a 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. Dependence of the reaction rate on hydrogen-ion concentration

[Aldehyde]: 0.10 mol dm ⁻³	[QCC]: 0.001 mol dm ⁻³				Temperature: 298 K	
[TsOH]/ mol dm ⁻³	0.10	0.20	0.40	0.60	0.80	1.00
10 ⁴ k _{obs} /s ⁻¹	9.18	10.8	13.5	16.2	18.9	22.5

Table 3. Rate constants and activation parameters of the oxidation of aliphatic aldehydes – QCC complexes.

R	10 ⁴ k ₂ (dm ³ mol ⁻¹ s ⁻¹)				ΔH*, kJ mol ⁻¹	-ΔS*, J mol ⁻¹ K ⁻¹	ΔG*, kJ mol ⁻¹
	288	298	308	318			
H	1.48	3.60	7.92	18.0	60.5±0.6	108±2	92.7±0.4
Me	20.7	45.9	90.9	189	53.2±0.6	112±2	86.4±0.5
Et	35.1	77.4	144	297	50.9±0.9	115±3	85.2±0.8
Pr	38.7	80.1	153	315	50.3±0.9	117±3	85.0±0.7
Pr ⁱ	57.8	117	234	459	50.3±0.9	117±3	85.0±0.7
ClCH ₂	0.072	0.20	0.49	1.26	69.7±0.7	102±2	99.8±0.6
MeCDO	3.42	7.29	15.3	32.4	54.4±0.7	123±2	90.9±0.6
k _H /k _D	6.01	5.78	5.63	5.38			

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 3).

Effect of acidity

The reaction is catalysed by hydrogen ions (Table 2). The hydrogen-ion dependence has the following form $k_{\text{obs}} = a + b[\text{H}^+]$. The values of a and b , for acetaldehyde, are $1.81 \pm 0.46 \times 10^{-4} \text{ s}^{-1}$ and $3.23 \pm 0.76 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($r^2 = 0.9978$).

$$\text{Rate} = k_2[\text{QCC}][\text{Aldehyde}] + k_3[\text{QCC}][\text{Aldehyde}][\text{TsOH}]$$

(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 QCC 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 of formation constants K and of decomposition constants of the complex, k_2 are recorded in Table 5.

Discussion

There is a fair correlation between the activation enthalpies and entropies of the oxidation of aldehydes ($r^2 = 0.9782$), indicating the operation of a compensation effect¹³. 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 method¹⁴. An Exner's plot between $\log k_2$ at 288 K and at 318 K was linear ($r^2 = 0.9992$) (Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is $882 \pm 25 \text{ K}$. 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.

Solvent effect

The rate constants, k_2 , in eighteen solvents (CS₂ 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.¹⁵

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

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 Eqns. 7-10.

$$\log k_2 = -3.97 + 1.41(\pm 0.17)\pi^* + 0.20(\pm 0.14)\beta +$$

$$0.15(\pm 0.13)\alpha \quad (7)$$

$$R^2 = 0.8681; \text{sd} = 0.16; n = 18; \psi = 0.39.$$

$$\log k_2 = -4.01 + 1.47(\pm 0.17)\pi^* + 0.15(\pm 0.11)\beta \quad (8)$$

$$R^2 = 0.8559; \text{sd} = 0.16; n = 18; \psi = 0.40$$

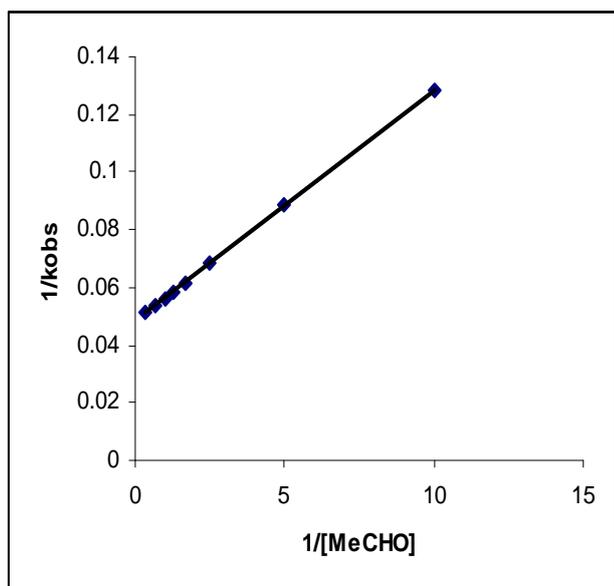


Figure 2. – Oxidation of Aldehyde by QCC: A double reciprocal plot

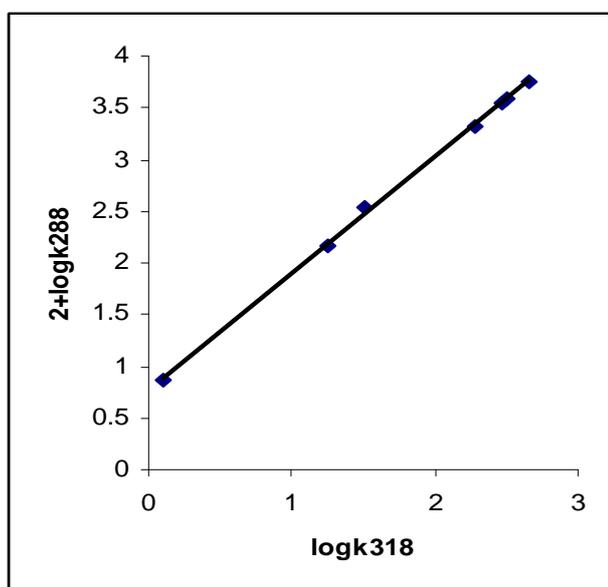


Figure 3. Exner's Isokinetic Relationship in the oxidation of Aldehydes by QCC

$$\log k_2 = -3.98 + 1.51(\pm 0.16)\pi^* \quad (9)$$

$$r^2 = 0.8437; \text{sd}=0.16; n=18; \psi=0.41$$

$$\log k_2 = -3.15 + 0.42(\pm 0.33)\beta \quad (10)$$

$$r^2=0.0806; \text{sd}=0.39; n=18; \psi=0.98$$

Here n is the number of data points and ψ is the Exner's statistical parameter.¹⁶

Kamlet's¹⁵ triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion¹⁶ the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 84% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation¹⁷ of cation- and anion-solvating concept of the solvents also as equation (11).

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

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 analysed in terms of equation (8), separately with A and B and with $(A+B)$.

$$\log k_2 = 0.61(\pm 0.09)A + 1.60(\pm 0.06)B - 4.24 \quad (12)$$

$$R^2 = 0.9765; \text{sd} = 0.07; n = 19; \psi = 0.07$$

$$\log k_2 = 0.39(\pm 0.53)A - 3.14 \quad (13)$$

$$r^2 = 0.0298; \text{sd} = 0.43; n = 19; \psi = 0.86$$

$$\log k_2 = 1.55(\pm 0.12)B - 4.04 \quad (14)$$

$$r^2 = 0.9091; \text{sd} = 0.18; n = 19; \psi = 0.32$$

$$\log k_2 = 1.27 \pm 0.14(A+B) - 4.21 \quad (15)$$

$$r^2 = 0.8369; \text{sd}=0.18; n = 19; \psi = 0.41$$

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.* 97% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by $(A+B)$, also accounted for *ca.* 83% of the data. In view of the fact that solvent polarity is able to account for *ca.* 80% 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 ($r^2 = 0.5253; \text{sd} = 0.30; \psi = 0.66$).

Correlation analysis of reactivity

The rates of the oxidation of six aldehydes show an excellent correlation with Taft's σ^* substituent constants,¹⁸ 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 4. Formation constants and thermodynamic parameters of the oxidation of aliphatic aldehydes – QCC complexes.

R	$10^4 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				ΔH^\ddagger , kJ mol ⁻¹	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹	ΔG^\ddagger , kJ mol ⁻¹
	288	298	308	318			
H	5.85	5.23	4.57	3.96	12.40.4	201	6.560.3
Me	6.03	5.45	4.79	4.15	12.00.5	180	6.570.4
Et	5.56	4.92	4.33	3.70	12.70.4	221	6.420.3
Pr	5.32	4.72	4.05	3.42	13.70.6	252	6.290.4
Pr ⁱ	5.94	5.30	4.65	4.05	12.20.3	191	6.600.3
ClCH ₂	6.12	5.50	4.85	4.32	11.40.2	161	6.690.2
MeCDO	5.67	5.15	4.52	3.85	12.70.5	212	6.520.4

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

Solvents	K , dm ³ mol ⁻¹	k_{obs} , s ⁻¹
Chloroform	6.03	14.8
Toluene	5.84	5.25
1,2-Dichloroethane	5.85	18.2
Acetophenone	5.45	20.0
Dichloromethane	5.90	15.8
THF	5.26	9.77
DMSO	5.45	45.9
t-Butylalcohol	5.15	7.24
Acetone	6.12	17.0
1,4-Dioxane	5.34	8.51
DMF	5.38	27.5
1,2-Dimethoxyethane	5.67	5.62
Butanone	5.90	12.0
CS ₂	5.89	1.57
Nitrobenzene	5.88	22.4
Acetic acid	5.50	3.34
Benzene	6.15	5.25
Ethyl Acetate	5.19	7.76
Cyclohexane	5.18	0.85

Table 6. Temperature dependence of the reaction constant

Temp.	288 K	298 K	308 K	318 K
ρ^\ddagger	-2.34±0.01	-2.24±0.02	-2.15±0.01	-2.06±0.05
r^2	0.9999	0.9998	0.9999	0.9989
SD	0.003	0.009	0.009	0.006
ψ	0.01	0.02	0.01	0.04

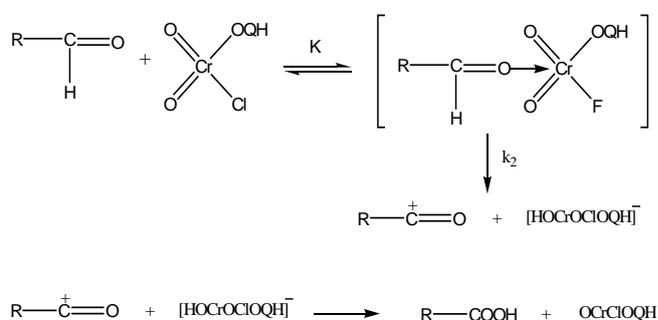
Mechanism

The observed hydrogen-ion dependence suggests that the reaction follows the two mechanistic pathways, one is acid-independent and the other is acid dependent. The acid-catalysis may well be attributed to a protonation of QCC to give a stronger oxidant and electrophile (16). Both QCC and QCCH⁺ are reactive species with the protonated form being more reactive.



Formation of a protonated Cr(VI) species has earlier been reported in the reactions of structurally similar halochromates.⁷⁻¹⁰

In aqueous solutions most aliphatic aldehydes exist predominantly in the hydrate form¹⁹ 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 ($k_{\text{H}}/k_{\text{D}} = 5.78$ 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.



Scheme - 1

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.

Conclusion

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 QCC are the reactive oxidising species. An aldehydic C-H bond is cleaved in the rate-determining step.

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