

A KINETIC AND MECHANISTIC STUDY SOME ALIPHATIC ALDEHYDES

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Abstract- The kinetics of oxidation reactions and the investigation of the reaction mechanisms from the kinetic data have been always the most interesting subjects in chemistry. In any kinetic investigation, one may be interested to arrive at (i) the relationship between the rate and the various factors like concentrations of the reactants, temperature, reaction medium etc., and (ii) interpretation of the empirical rate laws in the light of the mechanism proposed. Kinetic and mechanistic studies of the oxidation of aliphatic aldehydes, (in organic non-aqueous solvents), were discussed with an emphasis of correlation of structure and reactivity. 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: $k_{obs} = a + b [H^+]$. 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.

KEYWORD: - aliphatic aldehydes, correlation analysis, quinolinium chlorochromate, kinetics, mechanism, oxidation.

INTRODUCTION-

Selective oxidation of organic compounds under nonaqueous conditions is an important transformation in synthetic organic chemistry. Large quantities of aldehydes are directly emitted into the atmosphere from biogenic and anthropogenic sources and are also

produced in the atmosphere as intermediates in the photooxidation of volatile organic compounds (Papagni et al., 2000). Recently, several saturated aliphatic aldehydes have been identified and quantified in on-road vehicle emissions (Grosjean et al., 2001). Various halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry (Corey et.al 1975). Quinolinium chlorochromate (QCC) is one such compound used for the oxidation of compounds of industrial importance (Singh et.al. 1986). Oxidation of substituted benzaldehydes with various oxidants is an intensively studied area as well (Banerji et.al. 2012). We have been interested in the kinetic and mechanistic aspects of the oxidation by complexes Cr (VI) species and several reports on halochromates have already been reported from our laboratory (Vadera et.al. 2010. Sharma et.al. 2012). There seems to be only a few reports on the oxidation aspects of QCC are available in literature (Khatri et. al. 2012). 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.

MATERIAL & METHODS

QCC was prepared by the reported method 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 (Mitchell 1954). 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 (Perrin et.al. 1966).

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1 mol) and QCC (1.88 g, 0.01 mol) were dissolved in DMSO (100 ml) and the reaction mixture was allowed to stand for ca. ≈ 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 calorimetrically as Fe(III) hydroxamate by the procedure of Hall and Schaefer (Hall et. al. 1954). 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

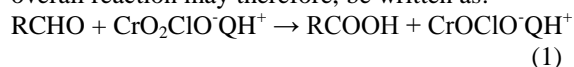
Pseudo-first-order conditions were attained by keeping an excess (± 15 or greater) of the [aldehyde] over [QCC]. The solvent was DMSO, unless mentioned otherwise. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reactions were carried out 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 $\log [QCC]$ 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: $k_2 = k_{obs}/[\text{aldehyde}]$.

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:



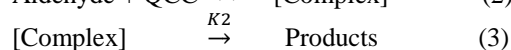
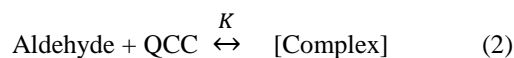
QCC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has

already been shown that both pyridinium chlorochromate (PCC) (Bhattacharjee et. al. 1987) and pyridinium fluorochromate (PFC) (Brown et. al. 1979) 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).

A plot of $1/k_{obs}$ against $1/[\text{aldehyde}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate. 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).

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

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.

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 $k_{obs} = a + b[H^+]$. 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 ($r_2 = 0.9978$).

Rate = $k_2[QCC][Aldehyde] + k_3[QCC][Aldehyde][TsOH]$ - (5)

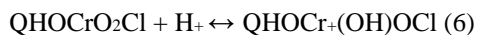
Effect of solvents

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 4.

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 (6). Both QCC and $QCCH^+$ are reactive species with the protonated form being more reactive.



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 ($k_H/k_D = 5.78$ 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. 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.

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

$10^3 [QCC]$ mol dm^{-3}	$[MeCHO]$ mol dm^{-3}	$[TsOH]$ mol dm^{-3}	$10^4 k_{obs}$ 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 mol dm⁻³ acrylonitrile

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^\ddagger , kJ mol ⁻¹	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹	ΔG^\ddagger , 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	18.9	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	3.41	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			

Table 4. Effect of solvents on the oxidation of acetaldehyde-QCC complex at 298 K

Solvent	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	22.4
CS ₂	5.89	12.0
Nitrobenzene	5.88	1.57
Acetic acid	5.50	22.4
Benzene	6.15	3.34
Ethyl Acetate	5.19	5.25
Cyclohexane	5.18	0.85

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 oxidizing species. An aldehydic C-H bond is cleaved in the rate determining step.

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