Kinetics and Mechanism of Oxidation of *para*-Substituted Benzaldehydes by Quinolinium Bromochromate in Aquo-acetic Acid Medium

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Oxidation of *para* substituted benzaldehydes by quinolinium bromochromate (QBC) leading to corresponding benzoic acids is first order with respect to QBC and the benzaldehydes while second order with respect to [H^+]. The oxidation of deuterated benzaldehyde exhibits a substantial primary kinetic isotope effect. The decreasing order of reactivity in low acidic solution for the benzaldehydes is p-NO_2 > p-Cl > H > p-OH > p-OCH_3. The results of correlation analyses point to an electron deficient reaction centre in the transition state. Formation of chromic-ester between hydrated benzaldehydes and protonated quinolinium bromochromate, followed by C—H bond fission in rate determining step, has been suggested. Activation parameters have also been evaluated.

Key Words: Kinetics, Oxidation, *para*-Substituted benzaldehydes, QBC.

INTRODUCTION

A large number of complexed Cr(VI) compounds as oxidizing agents have been reported. Mahanti and Banerji[1] reviewed synthetic and mechanistic aspects of reactions of complexed Cr(VI) compounds. Oxidation of substituted benzaldehydes by quinolinium fluorochromate (QFC)[2], pyridinium fluorochromate (PFC)[3] and quinolinium dichromate (QDC)[4] in aqueous acetic acid solution and PFC[5] in DMSO has been reported. Pandurangan *et al.*[6] first reported quinolinium bromochromate (QBC). But, so far no kinetic studies have been reported on its reactions as an oxidant. The preliminary experiment in our laboratory has shown contradiction to the results reported by Elango and Karunakaran[2] in the oxidation of benzaldehydes by QFC. The present paper reports the results on oxidation of benzaldehyde and substituted benzaldehydes by QBC in aquo-acetic acid medium.

EXPERIMENTAL

All the aldehydes and other chemicals used were of 'AnalaR' grade. Refluxing over CrO_3 followed by distillationof triethyl borate and acetic anhydride obtained with purified acetic acid. Deuterated benzaldehyde was obtained from Sigma

Chemicals. The standard solutions of different purified bezaldehydes and QBC were prepared in purified acetic acid. QBC was prepared by reported method[6] and crystallized from acetonitrile solution. Its purity was checked iodometrically and by m.p.

The reactions were followed under pseudo first order conditions keeping a large excess ($\times 10$) of the benzaldehydes over QBC. Concentration of QBC was followed iodometrically. The rate constants k_{obs} were computed from the linear plots of log [hypo] *vs.* time by least-square method. The results were reproducible to $\pm 2\%$.

Products of the oxidation were identified to be the corresponding benzoic acids and Cr(III). Stoichiometry investigations revealed that 3 moles of benzaldehyde consume 2 moles of QBC.

$$3C_6H_5CHO + 2Cr(VI) + 3H_2O \longrightarrow 3C_6H_5COOH + 2Cr(III) + 6H^+$$
$$\text{(2 moles QBC)}$$
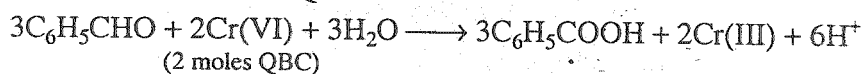
The reaction system failed to induce the polymerization of added acrylonitrile under inert atmosphere (N_2) suggesting the absence of free radical intermediate in the reaction.

RESULTS AND DISCUSSION

Stability of the oxidant (QBC) in solution

Solution of oxidant (QBC) in acetic acid-water-perchloric acid mixture obeys Beer-Lambert's law at λ_{max} 353 nm. There was no change in optical density and spectra of QBC solution in acetic acid-water-perchloric acid mixture on long standing or heating up to 60°C. The addition of quinoline has no effect on rate of reaction.

Effect of oxidant concentration on rate

At fixed [H⁺] with benzaldehyde in excess, the plot of log [QBC] *vs.* time was linear in individual runs up to 60–70% of the reaction indicating first order in QBC. The observed rate constants were independent of the initial concentration of QBC in all the benzaldehydes.

Effect of substrate concentration on rate

The rate of reaction increased with increase in concentration of benzaldehydes (Table-1). Plot of k_{obs} *vs.* [sub] gave linear line passing through origin. This indicates that no stable complex is formed and does not obey Michaelis-Menten type kinetics as suggested by Agarwal *et al.*[5] in oxidation by PFC. Plot of log k_{obs}. *vs.* log [sub] is also a straight line in all the cases with slope *ca.* 1 (for benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, *p*-hydroxy benzaldehyde, *p*-methoxybenzaldehyde are 0.96, 1.02, 1.25, 1.08 and 0.92 respectively).

Effect of ionic strength on rate

There was no effect of $NaNO_3$, Na_2SO_4 and $NaClO_4$ concentration on rate of reaction. This indicates the absence of ion-ion interaction in rate-determining step[7].

Effect of solvent composition on rate

At constant [H⁺], the rate of oxidation increased with increase in percentage

of acetic acid in solvent composition (Table-1). In other words, a decrease in rate is observed with increase in dielectric constant. Plot of log k_{obs} *vs.* $(D + 1)/(2D-1)$ is a curve suggesting the absence of dipole-dipole type of interaction step[7]. A plot of log k_{obs} *vs.* 1/D (dielectric constant) with positive slope > 20 (for benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde are 33.84, 41.66, 38.46, 33.07 and 51.90 respectively) indicating cation-dipole type of interaction[8].

TABLE-1

VARIATION OF RATE WITH SUBSTRATE CONCENTRATION, SOLVENT
COMPOSITION AND ADDED PERCHLORIC ACID

(Temprature = 303 K)

10^2 [Substrate] (mol dm^{-3})	AcOH % (v/v)	10 [H$^+$] (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})				
			-H	*p*-NO$_2$	*p*-Cl	*p*-OH	*p*-OCH$_3$
2.0	30	7.0	9.6	43.1	25.5	3.2	3.1
2.4	30	7.0	11.5	57.5	30.7	3.5	3.9
2.8	30	7.0	13.0	64.1	38.3	4.3	4.4
3.2	30	7.0	15.1	75.3	42.1	4.8	5.3
3.6	30	7.0	17.2	83.3	46.0	5.3	5.7
4.0	30	7.0	19.3	94.1	50.1	6.2	7.1
4.4	30	7.0	21.1	102.4	54.2	7.2	7.6
2.4	30	0.0	0.09	0.16	0.12	0.032	0.002
2.4	30	0.2	0.12	0.27	0.18	0.039	0.027
2.4	30	0.4	0.19	0.52	0.28	0.055	0.037
2.4	30	0.6	0.25	0.81	0.43	0.075	0.06z
2.4	30	0.8	0.31	1.15	0.66	0.106	0.085
2.4	30	1.0	0.40	1.95	0.88	0.136	0.131
2.4	30	2.0	1.11	4.98	2.05	0.369	0.353
2.4	30	3.0	2.41	11.62	6.35	0.717	0.751
2.4	30	4.0	4.11	18.51	10.23	1.231	1.252
2.4	30	5.0	6.13	28.73	15.36	1.923	1.952
2.4	30	6.0	7.91	42.28	23.60	2.654	2.811
2.4	30	8.0	15.13	72.21	43.37	4.821	4.954
2.4	30	10.0	22.29	115.15	65.73	7.154	7.602
2.4	30	12.0	33.19	163.51	94.99	10.449	10.911
2.4	20	7.0	9.8	47.9	25.8	3.1	2.9
2.4	25	7.0	10.4	52.5	28.0	3.2	3.3
2.4	35	7.0	12.4	63.1	33.2	3.9	4.4
2.4	40	7.0	13.7	69.1	38.1	4.3	5.1
2.4	50	7.0	17.4	102.4	49.1	5.7	8.1
2.4	60	7.0	24.2	159.4	69.1	7.6	11.7

Effect of perchloric acid concentration on rate

Rate of oxidation increased with increase in hydrogen ion concentration (Table-1). A plot of k_{obs} *vs.* $[H^+]^2$ was found to be linear passing through origin. A plot log k_1 *vs.* log $[H^+]$ was also linear in the range $[H^+] = 0.1–1.2$ mol dm^{-3} with slope *ca.* 2 (for benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde are 1.86, 2.00, 1.83, 1.96 and 1.86 respectively). The second order with respect to $[H^+]$ suggests an interaction between hydrated benzaldehydes and protonated QBC forming an ester, which then decomposes in a slow step forming corresponding benzoic acids. Ramakrishnan and Chockalingam[9] also suggested the reaction of hydrated benzaldehyde and protonated pyridinium fluorochromate in the oxidation of substituted benzaldehyde. In oxidation of benzaldehydes by $Cr(VI)$[10] and by bromine[11] involvement of hydrated benzaldehyde has also been suggested. The observations are inconsistent with the first order dependence on H^+ in oxidation of benzaldehydes by QFC[2], PFC[3] and QDC[4]. Bunnett hypothesis[12] and Bunnett-Olson's criterion[13] were also applied but slopes of the plots do not fit in the criterion. Probably it is due to involvement of large number of equilibria.

Kinetic isotope effect

The oxidation of 1-deuterated benzaldehyde by QBC was investigated to ascertain the C—H cleavage in the slow step. The rates of oxidation of benzaldehyde and 1-deuterated benzaldehyde, at 0.024 mol dm^{-3} [aldehyde], 0.7 mol dm^{-3} [$HClO_4$], 0.0024 mol dm^{-3} [QBC], $AcOH : H_2O = 70 : 30$ (v/v) and temperature 303 K are 1.15×10^{-4} (sec^{-1}) and 0.22×10^{-4} (sec^{-1}) respectively. Observed primary kinetic isotope effect ($k_H/k_D = 5.22$) at 303 K indicates that C—H bond cleavage occurs in slow step.

Thermodynamic parameters

To calculate various thermodynamic parameters, the rate constants were measured at 288 K to 323 K. The entropy of activation ranges within −84.85 to −121.84 J mol^{-1} K^{-1} (Table-2) for the oxidation of benzaldehydes by QBC suggesting that the oxidation involves the rupture of C—H bond in rate determining step, which is further confirmed by primary hydrogen isotope effect ($k_H/k_D = 5.22$) in the oxidation of benzaldehyde by QBC.
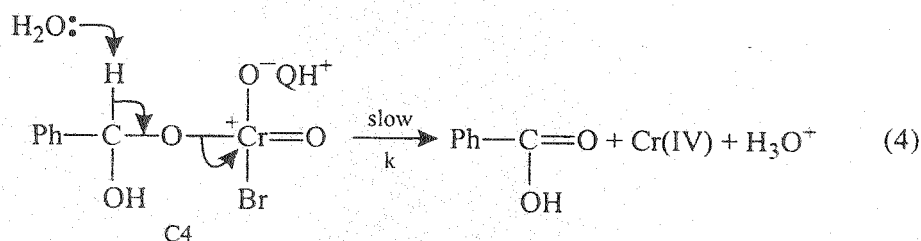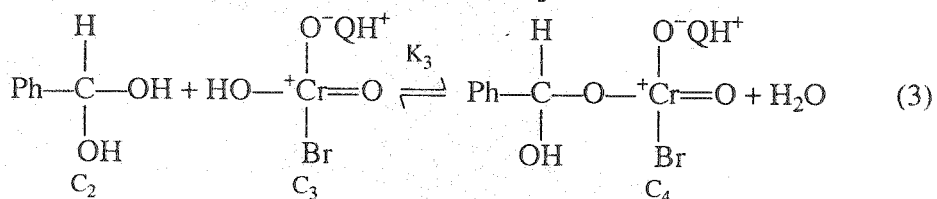
TABLE-2
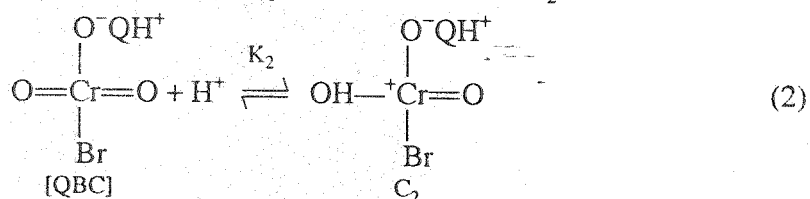THERMODYNAMIC PARAMETERS

Aldehyde	Energy of activation $\Delta E_a^{\neq}$ (kJ mol^{-1})	Entropy of activation $\Delta S^{\neq}$ (J mol K^{-1})	Free energy $\Delta G^{\neq}$ (kJ mol^{-1})
Benzaldehyde	61.47 ± 1.22	−84.18 ± 2.32	87.78 ± 2.95
p-Nitrobenzaldehyde	51.38 ± 1.20	−108.16 ± 2.71	84.15 ± 2.71
p-Chlorobenzaldehyde	51.86 ± 1.26	−111.04 ± 3.08	85.50 ± 2.76
p-Hydroxybenzaldehyde	58.59 ± 1.34	−106.90 ± 3.05	90.98 ± 2.85
p-Methoxybenzaldehyde	58.59 ± 1.34	−105.90 ± 3.05	90.70 ± 2.82

Effect of substituents on rate of reaction

Under identical experimental conditions, the rate of oxidation of benzaldehyde and substituted benzaldehydes follow the order: p-NO$_2$ > p-Cl > H > p-OH > p-CH$_3$O. The Hammett's plot of log k_{obs} $vs.$ α*[14] is linear with a reaction constant ρ = + 1.103 and correlation coefficient r = 0.95. The positive reaction constant ρ indicates the creation of carbocation in the transition state. Hence, the substituent, which can increase the magnitude of the positive charge on the carbonyl carbon of the benzaldehyde would (i) increase stability of the diol, $i.e.$, hydrated aldehyde formed, (ii) increase concentration of the diol and (iii) stabilize the transition state and cause an increase in the rate. The positive reaction constant ρ also supports the loss of aldehyde hydrogen atom as a proton in the slow step. If it is so, a better correlation must be observed in the plot of log k_{obs} $vs.$ σ^+. This has been found to be so with ρ = + 0.727 and an improved correlation coefficient r = 0.97. The higher rate of oxidation of p-nitrobenzaldehyde could be due to combined –I and –R effect, indicating more positive charge on carbonyl carbon atom. In p-chlorobenzaldehyde, a chloro group is capable of exerting –I and +R effect from p-position and this explains the order of reactivity observed (p-NO$_2$ > p-Cl > H). Similar effects, $i.e.$, electron attracting substituents increase the rate and electron donating substituents retard the rate of oxidation of aromatic aldehydes, has been observed by Lucchi[15] in Cr(VI), Hiran et $al.$[16] in peroxydisuphate and Aruna et $al.$[4] in QDC.

Considering all these experimental data, the following reaction scheme may be suggested:

$$
\underset{\substack{|\\ \text{Ph—C}=\text{O}}}{\overset{\text{H}}{}} + \text{H}^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\substack{C_1}}{\overset{\text{H}}{\underset{|}{\text{Ph—C}^+\text{—OH}}}} \xrightarrow[\text{H}_2\text{O}]{k'} \underset{\substack{|\\ \text{OH}\\ C_2}}{\overset{\text{H}}{\underset{|}{\text{Ph—C—OH}}}} + \text{H}^+ \qquad (1)
$$

$$
\underset{\substack{|\\ \text{Br}\\ [\text{QBC}]}}{\overset{\text{O}^-\text{QH}^+}{\underset{|}{\text{O}=\text{Cr}=\text{O}}}} + \text{H}^+ \overset{K_2}{\rightleftharpoons} \underset{\substack{|\\ \text{Br}\\ C_2}}{\overset{\text{O}^-\text{QH}^+}{\underset{|}{\text{OH—}^+\text{Cr}=\text{O}}}} \qquad (2)
$$

$$
\underset{\substack{|\\ \text{OH}\\ C_2}}{\overset{\text{H}}{\underset{|}{\text{Ph—C—OH}}}} + \underset{\substack{|\\ \text{Br}\\ C_3}}{\overset{\text{O}^-\text{QH}^+}{\underset{|}{\text{HO—}^+\text{Cr}=\text{O}}}} \overset{K_3}{\rightleftharpoons} \underset{\substack{|\\ \text{OH}}}{\overset{\text{H}}{\underset{|}{\text{Ph—C—O—}}}}\underset{\substack{|\\ \text{Br}\\ C_4}}{\overset{\text{O}^-\text{QH}^+}{\underset{|}{^+\text{Cr}=\text{O}}}} + \text{H}_2\text{O} \qquad (3)
$$

$$
\text{H}_2\text{O:}
$$

$$
\underset{\substack{|\\ \text{OH}\quad\text{Br}\\ C4}}{\overset{\text{H}\qquad\quad\text{O}^-\text{QH}^+}{\underset{|}{\text{Ph—C—O—}^+\text{Cr}=\text{O}}}} \xrightarrow[k]{\text{slow}} \underset{\substack{|\\ \text{OH}}}{\overset{\text{H}}{\underset{|}{\text{Ph—C}=\text{O}}}} + \text{Cr(IV)} + \text{H}_3\text{O}^+ \qquad (4)
$$

$$Cr(IV) + Cr(VI) \xrightarrow{\text{Fast}} 2Cr(V) \tag{5}$$
$$\underset{(QBC)}{}$$

$$2Cr(V) + 2PhCHO + 2H_2O \xrightarrow{\text{Fast}} 2PhCOOH + 2Cr(III) + 4H^+ \tag{6}$$
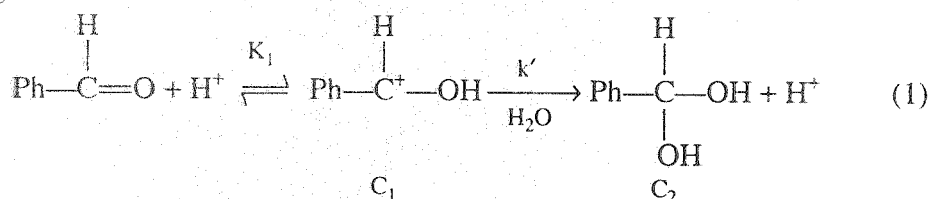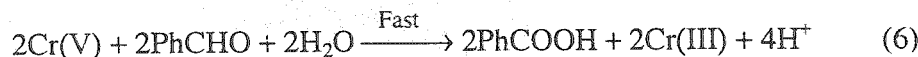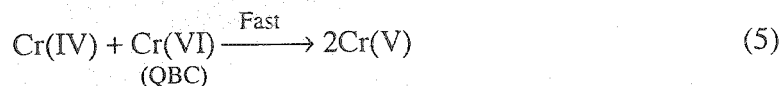
The interaction of C_3 with C_1 can be ruled out, as there was no effect of ionic strength on rate while solvent effect indicates cation-dipole type of interaction[8].

Based the on above mechanism, the rate laws can be derived as follows:

$$Rate = -\frac{d[QBC]}{dt} \, \alpha[C_4]$$

$$= k[C_4]$$

$$= kK_3[C_2][C_3]$$

$$= kK_3K_1k'[H^+][PhCHO] \cdot K_2[QBC][H^+]$$

$$= kk'K_1K_2K_3[PhCHO][H^+]^2[QBC]$$

$$= k_{obs}[QBC]$$

where $\quad k_{obs} = kk'K_1K_2K_3[PhCHO][H^+]^2 = k_s[PhCHO][H^+]^2$

and specific rate constant, k_s, as $\quad k_s = \dfrac{k_{obs}}{[PhCHO][H^+]^2}$.

This rate law is consistent with all the observed experimental results[17].

ACKNOWLEDGEMENT

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