Kinetics and Mechanism of Oxidation of *m-/p*-Nitrobenzaldehydes by Quinolinium Bromochromate in Acetic Acid-Perchloric Acid-Water Medium

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Oxidation of benzaldehyde, *p*-nitro- and *m*-nitrobenzaldehydes by quinolinium bromochromate (QBC) in aquo-acetic acid medium is first order each in QBC and benzaldehyde while second order with respect to H^+. The products of oxidation are the corresponding benzoic acids and Cr(III). The oxidation of deuterated benzaldehyde exhibits a substantial primary kinetic isotope effect. Formation of chromic-ester between hydrated benzaldehydes and protonated quinolinium bromochromate, followed by C—H bond fission in slow step, explains the observed experimental facts. The order of reactivity in benzaldehydes is $p\text{-}NO_2 > m\text{-}NO_2 > H$. Activation parameters for the observed rate constant have been evaluated.

Key Words: Kinetics, Oxidation, Nitrobenzaldehydes, Quinolinium bromochromate.

INTRODUCTION

Quinolinium bromochromate (QBC) as a Cr(VI) oxidant was chosen in view of its ease of preparation, stability in the medium, selective and mild oxidant in synthetic organic chemistry[1]. Mahanti and Banerji[2] have reviewed the synthetic, kinetic and mechanistic aspects of complexed Cr(VI) compounds. Oxidation of benzaldehydes by quinolinium fluorochromate[3], pyridinium chlorochromate[4] and quinolinium dichromate[5] in aquo-acetic acid medium and by pyridinium fluorochromate[6] in DMSO have been reported, but there seems to be no report on the kinetics of oxidation of benzaldehydes by QBC in aquo-acetic acid medium. Here we report the results on oxidation of substituted benzaldehydes by QBC in aquo-acetic acid medium.

EXPERIMENTAL

Materials and Methods: All the aldehydes and other chemicals were of 'AnalaR' grade. Acetic acid was purified as described by reported method[7]. Deuterated benzaldehyde was obtained form Aldrich Chemicals. The stock solution of benzaldehyde was prepared by dissolving known quantity of benzaldehyde in acetic acid and was estimated either by sodium bisulfate or hydroxylamine hydrochloride[8]. QBC was prepared by mixing 48% hydrobromic acid

(17 mL, 0.1 mole) with a stirred and cooled (273 K) solution of CrO_3 (10.0 g, 0.1 mol) in distilled water (20.0 mL) followed by mixing of quinoline (13.0 mL, 0.1 mol). The orange solid, which separated out, was filtered, washed with water, dried in vacuum and crystallized from acetonitrile. Its purity was checked iodometrically and m.p. (428 K). Structure was confirmed by elemental analysis (Found: C, 34.95; H, 2.58; N, 4.53; Calcd. for $C_9H_8NCrO_3Br$: C, 34.98; H, 2.56; N, 4.42%) and IR spectrum which exhibited band at (KBr) 955, 747, 605, 523, 465 and 383 cm^{-1}. Standard QBC solution was prepared in purified glacial acetic acid.

Kinetic measurements: The reactions were followed under pseudo first order conditions keeping a large excess (x10) of the benzaldehydes over QBC. Known volumes of substrate, perchloric acid and acetic acid were mixed in a reaction flask and kept in a thermostat maintained at constant temperature (± 0.1 K). The reaction was initiated by adding rapidly predetermined volume of QBC solution into the above reaction mixture. Aliquots (5.0 mL) were withdrawn at regular time intervals and added to 10 mL of 10% potassium iodide solution. This was titrated against previously standardized sodium thiosulphate (hypo) using starch as an indicator. The rate constants were computed from the linear plots of log [hypo] *vs.* time by least-square method. The results were reproducible to +5%. Orders with respect to different reactants were determined by Ostwald isolation method.

Product Study and Stoichiometry: Product of the oxidation was identified as benzoic acid. After completion of the reaction under kinetic conditions, the reaction mixture was treated with solid $NaHCO_3$. After complete neutralization, the reaction mixture was extracted with ether to remove unreacted benzaldehyde. Aqueous layer was treated with concentrated hydrochloric acid. The solid obtained was filtered, washed with cold water, dried, weighed and identified as benzoic acid by m.p. (mixed m.p.) and chemical test. Stoichiometric investigations revealed that 3 mol of benzaldehyde consume 2 mol of QBC. Hence the reaction is represented as:

$$3C_6H_5CHO + 2Cr(VI) + 3H_2O \longrightarrow 3C_6H_5COOH + 2Cr(III) + 6H^+$$
$$\text{(2 mol QBC)}$$
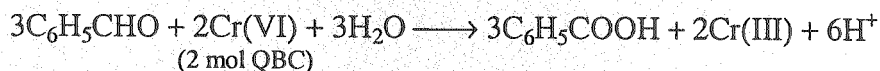
No polymerization of acrylonitrile was observed in the reaction mixture under inert atmosphere (N_2). There was no change in rate of reaction in the presence of acrylonitrile. This suggests that free radicals are not formed in the reaction.

RESULTS AND DISCUSSION

Solution of oxidant (QBC) in acetic acid-water-perchloric acid mixture obeys Beer-Lambert's law at λ_{max} 353 nm. In absence of benzaldehydes, the oxidant was stable in all the kinetic conditions, *i.e.*, no change in absorbance.

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

Effect of substrate: The rate of reaction increased with increase in concentration of benzaldehydes (Table-1). Plot of log k_{obs} *vs.* log [substrate] is linear in all the cases with slope *ca.* 1 (for benzaldehyde, *m*-nitrobenzaldehyde, *p*-nitrobenzaldehyde are 0.96, 1.08 and 1.02 respectively). Plot of $1/k_{obs}$ *vs.* 1/[substrate] gave linear line passing through origin. In the oxidation by PFC[6, 9] in DMSO Michaelis-Menten type kinetics were observed with respect to the aldehydes.

TABLE-1

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

[QBC] = 2.4×10^{-3} mol dm^{-3}; Temp. = 303 K

[Substrate] $\times 10^3$ (mol dm^{-3})	[HClO$_4$] $\times 10^1$ (mol dm^{-3})	CH$_3$COOH % (v/v)	$k_{obs} \times 10^5$ (s^{-1})		
			Benzaldehyde	*m*-Nitro benzaldehyde	*p*-Nitro benzaldehyde
1.0	7.0	30	4.6	9.9	20.8
2.0	7.0	30	9.6	20.4	43.1
2.4	7.0	30	11.5	25.5	57.5
2.8	7.0	30	13.0	28.2	64.1
3.2	7.0	30	15.1	33.2	75.3
3.6	7.0	30	17.2	36.6	83.3
4.0	7.0	30	19.3	41.6	94.1
4.4	0.0	30	21.1	47.3	102.4
2.4	0.2	30	0.09	0.13	0.16
2.4	0.4	30	0.12	0.24	0.27
2.4	0.6	30	0.19	0.39	0.52
2.4	0.8	30	0.25	0.55	0.81
2.4	1.0	30	0.31	0.81	1.15
2.4	2.0	30	0.40	0.98	1.95
2.4	3.0	30	1.11	2.83	4.98
2.4	4.0	30	2.41	5.51	11.62
2.4	5.0	30	4.11	9.15	18.51
2.4	6.0	30	6.13	13.53	28.73
2.4	8.0	30	7.91	19.19	42.28
2.4	10.0	30	15.13	33.51	72.21
2.4	12.0	30	22.29	51.25	115.15
2.4	7.0	30	33.19	74.81	163.51
2.4	7.0	20	9.8	20.9	47.9
2.4	7.0	25	10.4	22.7	52.5
2.4	7.0	35	12.4	27.5	63.1
2.4	7.0	40	13.7	30.7	69.1
2.4	7.0	50	17.4	41.3	102.4
2.4	7.0	60	24.2	69.1	159.4

Effect of perchloric acid: Rate of oxidation increased with increase in hydrogen ion concentration (Table-1). A plot of k_{obs} against $[H^+]$ is a curve turning asymptotic at higher $[H^+]$ (> 0.8 mol dm^{-3}) (Fig. 1). This suggests a dependence of k_{obs} on $[H^+]$ of the form:

$$k_{obs} = a + b[H^+] + c[H^+]^2 + \ldots$$

The smooth curve drawn cuts the rate ordinate near zero (Fig. 1). The value of 'a' is negligibly small. A plot of $(k_{obs} - a)/[H^+]$ *vs.* $[H^+]$ (assuming no
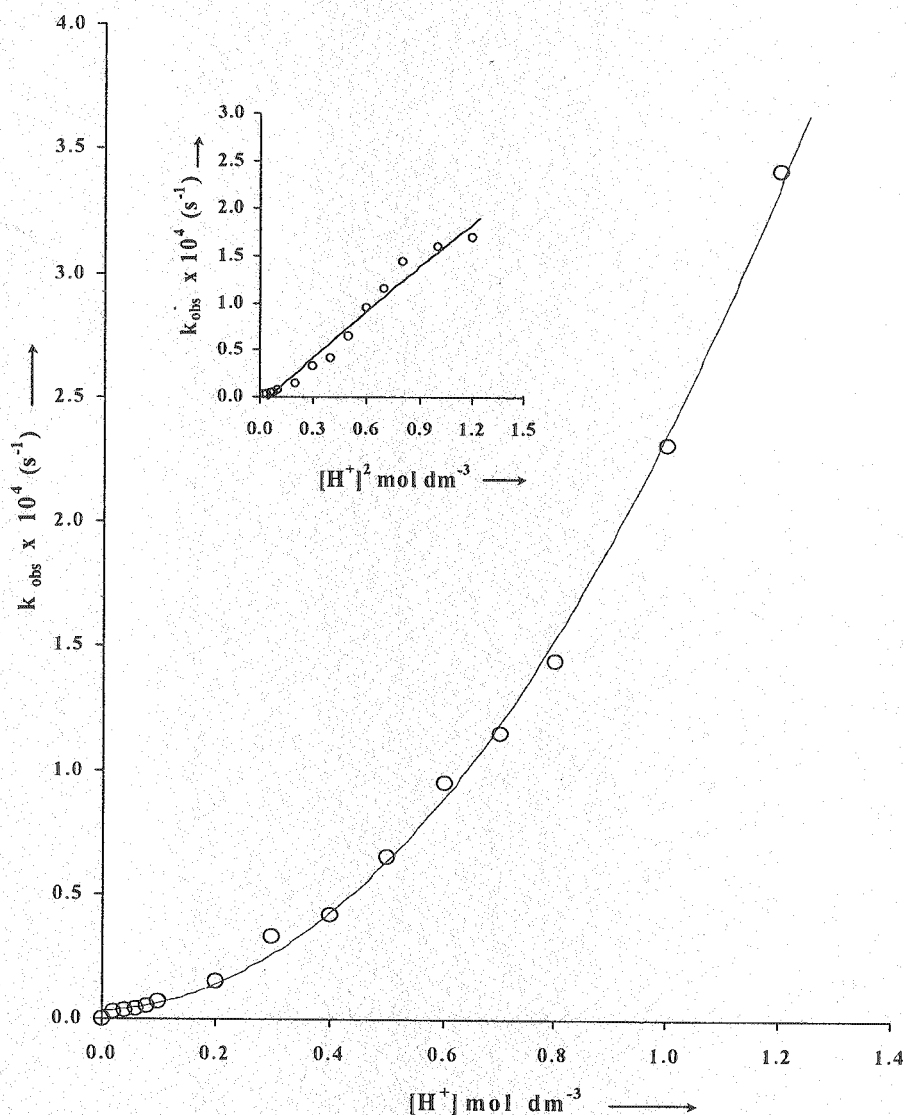

Fig. 1. Variation of rate with perchloric acid concentation at [benzaldehyde] = 2.4×10^{-2} mol dm^{-3}; [QBC] = 2.4×10^{-3} mol dm^{-3}; acetic acid = 30%(v/v); Temp. = 303 K

participation of higher order than 2 in $[H^+]$) should give a straight line with intercept equal to 'b' and slope equal to 'c' (Fig. 1, inset). Again the plot is a smooth curve, which passes through very near the origin. This also suggests that the value of 'b' is also small and can be neglected. Thus, the form of dependence

of rate constant on $[H^+]$ cannot be expressed in this polynomial form. A plot of k_{obs} *vs.* $[H^+]^2$ was, therefore, attempted and was found to be linear passing through origin. A plot log k_{obs} *vs.* log $[H^+]$ was also linear in the range $[H^+]$ + 0.1 to 1.2 mol dm^{-3} with slope *ca.* 2 (for benzaldehyde, *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde are 1.86, 1.96 and 2.00 respectively), indicating that rate is proportional to the square of hydrogen ion concentration. The dependence of rate on $HClO_4$ concentration, *i.e.*, order with respect to $[H^+]$, suggests an interaction between hydrated benzaldehydes and protonated QBC forming an ester, which then decomposes in rate determining step, catalyzed by water molecule forming corresponding benzoic acids. Bunnett's hypothesis[10] and Bunnett-Olsen[11] criterion could not be applied as no one plot gave ideal slope. This may be due to involvement of large number of equilibria. A protonated Cr(VI) species is likely to be a better electrofile and oxidant compared to the neutral one. Ramakrishnan and Chockalingam[12] also suggested the reaction of hydrated benzaldehyde and protonated pyridinium fluorochromate in the oxidation of substituted benzaldehydes by PFC. In oxidation of benzaldehydes by Cr(VI)[13] and by bromine[14] involvement of hydrated benzaldehyde has also been suggested.

Effect of ionic strength: 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[15]. Therefore ionic strength was not kept constant throughout the study.

Effect of solvent composition: At constant $[H^+]$, the rate of oxidation increased with increase in percentage of acetic acid in solvent composition (Table-1). In other words, with increase in dielectric constant there is a decrease in rate. Plot of log k_{obs} *vs.* $(D + 1)/(2D - 1)$ is a curve suggesting the absence of dipole-dipole type of interaction step[15]. A plot of log k_{obs} *vs.* 1/D (dielectric constant) with positive slope > 20 (for benzaldehyde, *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde are 33.84, 45.01 and 41.66, and 51.90 respectively) indicate cation-dipole type of interaction[16].

Effect of Mn(II) ion: It has been observed that addition of low concentration of Mn(II) ion retards the rate of oxidation (Table-2).

TABLE-2

A REPRESENTATIVE DATA OF EFFECT OF Mn(II) ION ON RATE

$[HClO_4]$ = 7.0 × 10^{-1} mol dm^{-3}; [benzaldehyde] = 2.4 × 10^{-2} mol dm^{-3}; [QBC]= 2.4 × 10^{-3} mol dm^{-3}; CH_3COOH = 30% (v/v); Temp. = 303 K

[Mn(II)] × 10^3 (mol dm^{-3})	k_{obs} × 10^5 (s^{-1})
0.0	11.5
2.0	8.6
4.0	8.1
6.0	5.9
8.0	5.1
10.0	4.6

This may be taken as evidence for formation of Cr(IV) species and hence QBC is acting as two-electron transfer oxidant. Thangara and Gopalan[17] also reported similar effect of Mn(II) ion in oxidation of 2-propanol by chromic acid in acetic acid-water medium and concluded chromic acid is acting as two-electron transfer oxidant.

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 deuterated benzaldehyde (PhCDO) at 0.024 mol dm^{-3} [aldehyde], 0.7 mol dm^{-3} [HClO$_4$], 0.0024 mol dm^{-3} [QBC], HOAc : H$_2$O = 70 : 30 (v/v) and temperature 303 K are 1.15×10^{-4} (s^{-1}) and 0.22×10^{-4} (s^{-1}) respectively. Observed primary kinetic isotope effect (k$_H$/k$_D$ = 5.22) at 303 K, confirming the C—H bond cleavage in the slow step.
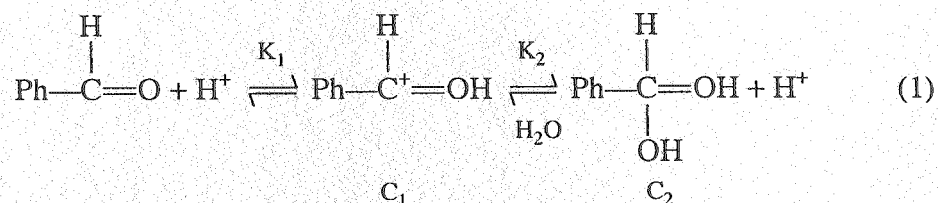
Effect of temperature: To calculate various thermodynamic parameters (Table-3), the rate constants were measured at 288 K to 323 K. The entropy of activation ranges within –84.85 to –121.84 J mol^{-1} K^{-1} (Table-3) for the oxidation of benzaldehydes by QBC suggest that the oxidation involves the rupture 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.
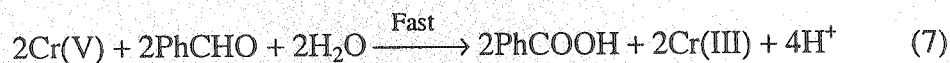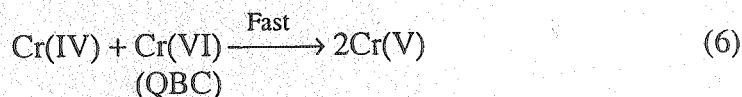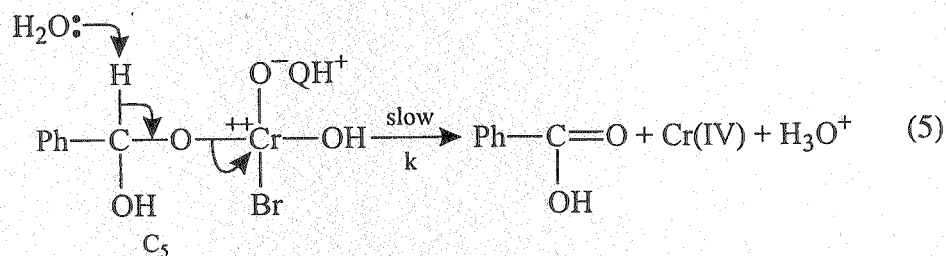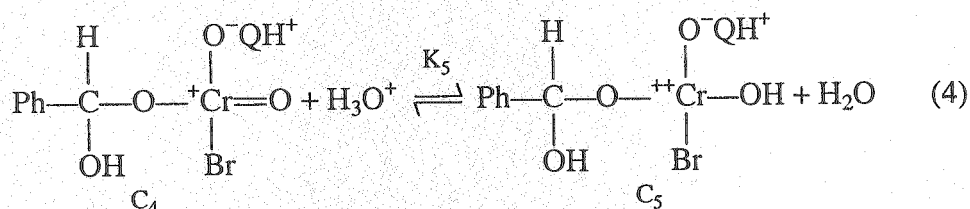
TABLE-3
THERMODYNAMIC PARAMETERS

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 ± 3.78	–84.18 ± 4.32	87.78 ± 4.95
m-Nitrobenzaldehyde	49.05 ± 2.14	–121.84 ± 6.18	85.96 ± 4.82
p-Nitrobenzaldehyde	51.38 ± 2.34	–108.16 ± 5.61	84.15 ± 4.21

Effect of substituents: Under identical experimental conditions, the rate of oxidation of benzaldehyde and substituted benzaldehydes follows the order: *p*-NO$_2$ > *m*-NO$_2$ > H. Hence, the substituents, which can increase the magnitude of the positive charge on the carbonyl carbon of the benzaldehyde would stabilize the transition state and cause an increase in the rate. The higher rate of oxidation of *p*-nitrobenzaldehyde could be due to combined –I and –R effects, indicating more positive charge on carbonyl carbon atom. In case of *m*-nitrobenzaldehyde, the only effect that is operative is the –I effect. This explains the order of reactivity observed (*p*-NO$_2$ *m*-NO$_2$ > H). Similar observations in aromatic aldehydes oxidation were reported by Lucchi[18] in Cr(VI), Aruna *et al.*[5] in QDC and Hiran *et al.*[19] in peroxydisulphate.

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

$$\underset{C_1}{\underset{\underset{H}{|}}{Ph-C=O}} + H^+ \overset{K_1}{\rightleftharpoons} \underset{\underset{H_2O}{}}{\underset{\underset{H}{|}}{Ph-C^+=OH}} \overset{K_2}{\rightleftharpoons} \underset{C_2}{\underset{\underset{OH}{|}}{\underset{\underset{H}{|}}{Ph-C=OH}}} + H^+ \qquad (1)$$

$$O=Cr=O + H^+ \underset{}{\overset{K_3}{\rightleftharpoons}} HO-{}^+Cr=O \qquad (2)$$

[QBC] C_2

$$Ph-\underset{OH}{\overset{H}{C}}-OH + HO-{}^+Cr=O \underset{}{\overset{K_4}{\rightleftharpoons}} Ph-\underset{OH}{\overset{H}{C}}-O-{}^+Cr=O + H^+O \qquad (3)$$

C_2 C_3 C_4

$$Ph-\underset{OH}{\overset{H}{C}}-O-{}^+Cr=O + H_3O^+ \underset{}{\overset{K_5}{\rightleftharpoons}} Ph-\underset{OH}{\overset{H}{C}}-O-{}^{++}Cr-OH + H_2O \qquad (4)$$

C_4 C_5

$$Ph-\underset{OH}{\overset{H}{C}}-O-{}^{++}Cr-OH \xrightarrow[k]{slow} Ph-\underset{OH}{\overset{}{C}}=O + Cr(IV) + H_3O^+ \qquad (5)$$

C_5

$$Cr(IV) + Cr(VI) \xrightarrow{Fast} 2Cr(V) \qquad (6)$$
(QBC)

$$2Cr(V) + 2PhCHO + 2H_2O \xrightarrow{Fast} 2PhCOOH + 2Cr(III) + 4H^+ \qquad (7)$$
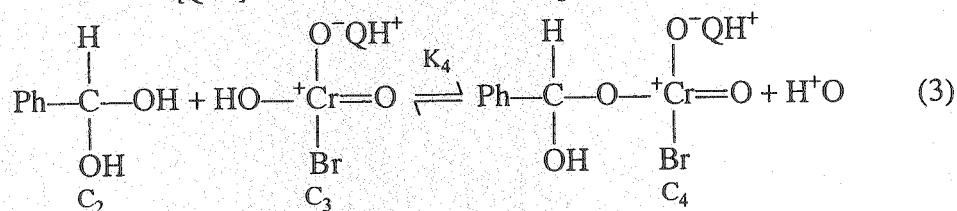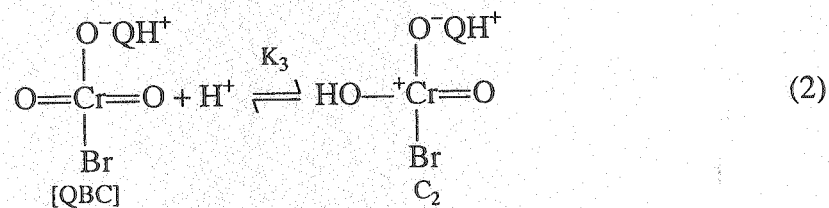
C_5 can also be formed by the interaction of C_3 with C_1. But the salt effect on the rate of reaction ruled out this possibility. C_4 can also lead to products but the observed second order rate with respect to H^+ rejects the possibility.

A transition state (C_6), consistent with the observed negative entropy, can also be speculated.

$$\left\{ Ph-\underset{OH}{\overset{H}{C}}-O-{}^+Cr=O-H^+ \right\}$$

C_6
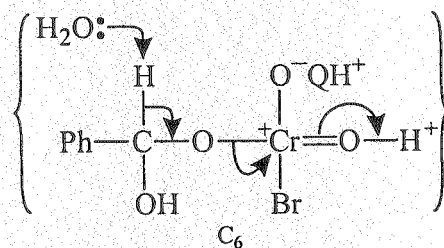
Based on the above mechanism, the rate laws can be derived as follows:

$$Rate = -\frac{d[QBC]}{dt} \propto [C_5]$$

$$= k[C_5]$$

$$= kK_5[C_4][H^+]$$

$$= kK_4K_5[C_2][C_3][H^+]$$

$$= kK_1K_2K_4K_5[PhCHO] \cdot K_3[QBC][H^+] \cdot [H^+]$$

$$= kK_1K_2K_3K_4K_5[PhCHO][QBC][H^+]^2$$

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

$$= k_1[QBC]$$

where $K_{obs} = kK_1K_2K_3K_4K_5[PhCHO][H^+]^2 = k_1$

$$= k_s[PhCHO][H^+]^2$$

and specific rate constant, k_s, as

$$k_s = \frac{k_{obs}}{[PhCHO][H^+]^2}$$

This rate law is consistent with all observed experimental results.

ACKNOWLEDGMENT

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