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REVIEW

Pyridinium and Quinolinium Halochromates: Kinetic and Mechanistic Aspects

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Heterocyclic halochromates, a new class of mild Cr(VI) reagents have been introduced recently as oxidizing agents for the oxidation of organic substrates. These reagents have been found to be better in their reactivity and selectivity compared to the common Cr(VI) oxidants. Pyridinium and quinolinium halochromates adds to the select list of newer Cr(VI) reagents as the most significant oxidants for the effective and selective oxidation of organic substrates under mild conditions. This review highlights the recent work done on the redox reactions of pyridinium and quinolinium halochromates from kinetic and mechanistic point of view and covers literature upto June 2010.

Key Words: Pyridinium halochromates, Quinolinium halochromates, Kinetic and Mechanistic studies, Review.

INTRODUCTION

The study of oxidation of organic compounds is of immense importance both from mechanistic and synthetic points of view. Hexavalent chromium compounds are highly valuable oxidants for the oxidation of organic and inorganic substrates. Many reviews and books are available which have dealt at lengths with the mode of action of Cr(VI) reagents[1-12]. The earlier known Cr(VI) oxidants such as chromium trioxide, chromyl chloride, Jones reagent *etc*. lacked mildness, operational simplicity, versatility and selectivity which are important prerequisites for an oxidant to be useful. This consideration has led to development of new Cr(VI) based reagents and associated methodologies. Consequently various Cr(VI) reagents, with ligands such as pyridine[13-16], quinoline[17-22] and 2,2'-bipyridine[23], 4-(dimethylamino)-pyridine[24], 1-methyl imidazole[25], isoquinoline[26], imidazole[27-29], γ-picoline[30], pyrazine[31], 3-carboxy-pyridine[32], benzimidazole[33] *etc*. have been developed. Among these Cr(VI) reagents pyridinium and quinolinium halochromates have been reported to be stable reagents. These reagents have been used as mild and selective oxidants in synthetic organic chemistry. Sufficient contributions have been made up-to now in the kinetics and mechanism of oxidation of organic substrates by pyridinium and quinolinium halochromates. This article presents the contribution on the oxidation reactions of organic substrates and pyridinium and quinolinium halochromates with emphasis on kinetics and mechanism.

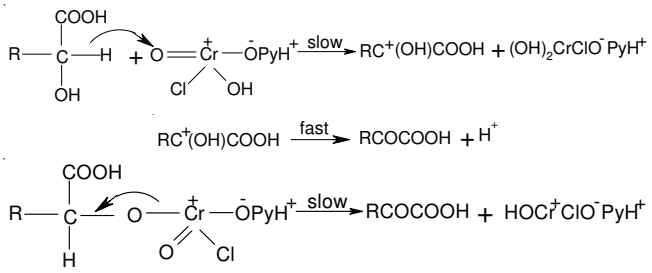
Oxidation kinetics with pyridinium halochromates

Oxidation kinetics with pyridinium chlorochromate (PCC): Among halochromates of nitrogen containing heterocyclic compounds, pyridinium chlorochromate is a versatile oxidizing agent. It has been widely used in organic synthesis[8].

Pyridinium chlorochromate (PCC) as a potential oxidant of primary and secondary alcohols was first reported by Corey and Suggs[13]. Kinetic studies on the oxidation of the primary alcohols by PCC have provided important information on the mechanism of the process[34]. Involvement of a protonated chromium species in the rate determining step is indicated by the catalysis of the reaction by the acid, the acid catalyzed reaction being nearly the first order. The involvement of a cationic transition state R-C^{+}HOH in the oxidation of primary alcohols was corroborated by the formation of ketone along with the expected aldehyde during oxidation[35]. The kinetics of oxidation of substituted benzhydrol[36] with PCC is first order in each reactant. Oxidation of benzyl alcohols[37], cyclopentanol[38] by PCC in nitrobenzene-chlorobenzene mixture have also been reported. The oxidation of benzhydrol[39] in DMSO and of 2-pentanol[40] in chloroform has been studied. Structure-reactivity corelation in the oxidation of some substituted oxan-4-ols by PCC have been investigated[41]. The uncatalyzed and perchloric acid catalyzed oxidation of unsaturated alcohols *viz.*, allyl alcohol, crotyl alcohol and cinnamyl alcohol by PCC in aqueous acetic acid medium leads to the formation of aldehydes. Both

the reactions are first order reactions each in [PCC] and [alcohol]. The rate determining step involves the participation of unprotonated PCC in uncatalyzed reaction and protonated PCC in perchloric acid catalyzed reaction[42].

The choice of hydroxy acids as substrates for the PCC oxidation studies is particularly interesting because of their bifunctionality. Banerji[43,44] favoured a hydride ion transfer in the rate determining step as shown below:



The oxidation of maleic acid, furmaric acid, crotonic acid and cinnamic acid by PCC in DMSO leads to the formation of corresponding epoxide. A mechanism involving a three centre transition state has been proposed[45].

Oxidation of lower oxyacids of phosphorus by PCC results in the formation of the corresponding higher oxyacids of phosphorus. Transfer of a hydride ion from the P-H bond to PCC, in the rate determining step, has been proposed[46].

Kinetics of PCC oxidation of Co(III)-bound and unbound α-hydroxy acid (mandelic acid and lactic acid) exhibits total second order kinetics-first order in each reactant[47].

Pyridinium chlorochromate (PCC) oxidizes carbonyl compounds to corresponding acids. The mechanism of oxidation of aldehydes[48] and disubstituted benzaldehydes[49] by Corey's reagents in binary solvent mixture of aqueous acetic acid is first order each in [aldehyde], [PCC] and [H^+].

There is definite inductive, resonance and steric effects that operates in the oxidation of *ortho*-substituted benzaldehydes with PCC[50]. Uncatalyzed and Ru(III) catalyzed oxidation of aliphatic aldehydes by PCC in aqueous acetic acid medium, has been studied. A mechanism involving the formation of complex between Ru(III) and substrate is proposed[51]. Oxidation of aliphatic aldehyde by PCC, in DMSO, to the corresponding carboxylic acids, is first order each in PCC, the aldehyde and hydrogen ions. A mechanism involving transfer of hydride ion has been suggested[52].

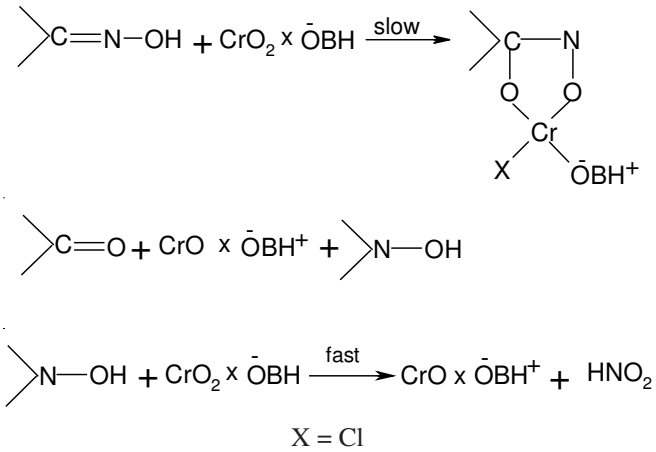
Mechanism of co oxidation of benzaldehyde and oxalic acid by PCC in 50 % acetic acid-50 % water (v/v) mixture involves the formation of cyclic ternary complex in a slow step[53].

The kinetics and mechanism of oxidation of oxalic acid[54] and thiodiglycollic acid[55] by PCC have been reported. Oxidation of formic acid and oxalic acid[56] and thioacids[57] by PCC using DMSO as the solvent, has been studied. The reactions exhibited Michaelis-Menten type kinetics with respect to the organic acids. Kinetics of co-oxidation of S-phenylmercapto acetic acid and oxalic acid with PCC exhibits a first order dependence each in [PCC] and [S-mercaptoacetic acid], at low concentrations of the later[58]. Kinetics of oxidation of S-arylmercaptoacetic acid by PCC have been studied in acidic medium. A mechanism involving the formation of protonated arylsulfinyl acetic acid intermediate, followed by an intermolecular rearrangement leading to the product thiophenol has been proposed[59].

The oxidation of a series of sulphides by PCC have been studied[60-65]. It has been proposed that the oxidation proceeds involving oxygen transfer from PCC to sulphide. Electron transfer from sulphur to Cr(VI) results in the formation of a polar transition state. The reaction between DMSO and PCC was found to proceed with an ester formation. The ester thus formed decomposes in a slow step to produce Cr(IV) which then oxidizes another DMSO molecule generating a free radical in a fast step[66]. Phosphorothionate derivative like malathion have also been subjected to oxidation by PCC[67].

The oxidation of methionine[68] by PCC has been studied. Results show that methionine is oxidized to the corresponding sulfoxide and behave like sulfide towards oxidant.

Kinetics of the oxidative regeneration of carbonyl compounds from oximes by PCC has been studied recently. The reactions exhibited first order dependence on both the oxidant and oxime. A mechanism involving the formation of a cyclic intermediate, in the rate determining step has been proposed[69].



X = Cl

The oxidation of diols is of particular interest from mechanistic point of view due to the fact that they are cleaved under mild conditions. Oxidation of pinacol[70] by PCC in dichloromethane-nitrobenzene mixture involves the C-C cleavage to give hydrogen bond gauche conformation. Both sturctural[71,72] and solvent influence leads to the conclusion that the reaction involves the removal of hydride ion, leaving a carbonium ion as a transient intermediate which undergoes further change to form the product. The oxidation of diols by PCC in DMSO results in the formation of corresponding carbonyl compound *via* chromate ester[73].

The oxidation of aromatic anil by PCC followed first order kinetics with respect to each of the reactant[74]. Interactive free energy relationship on the oxidation of aromatic anils by PCC have also been investigated[75].

Kinetics of several aromatic acetals with different substitutents in the benzene ring and alcohol moietis have been studied. An acyclic bimolecular transition state is proposed[76].

The kinetics of oxidation of 3-methyl-2,6-diphenyl-piperidin-4-one by PCC have been studied in DMSO,

1,4-dioxane, *t*-butanol and acetone. Solvent plays a dominant role on reactivity[77].

The oxidation of substituted styryl phenyl ketone and substituted methyl ketone[78], substituted styryl 4-biphenyl ketones and substituted 2-fluorenyl ketones[79] and phenyl styryl ketone[80] by PCC in 90 % acetic acid in the presence of perchloric acid, lead to the formation of epoxide.

The oxidation kinetics of some reducing sugars with PCC in perchloric acid medium has revealed a linear correlation between the observed rate and [sugar], [H^+]. A comparasion of D-glucose oxidation with its various C-1 and C-2 substituted derivatives shows that inductive, steric and shielding effect may all be important which explains the reactivity as 2-deoxy-D-glucose > D-glucose>1-O-methyl-α-glucopyranoside > 2-amino-2-deoxy-D-glucose hydrochloride. A comparasion between α- and β-anomers of some monosaccharides reveals that β-anomer is oxidized faster than α-anomer[81].

In the EDTA-catalyzed oxidation of cycloalkanes by PCC Cr(VI) EDTA-cycloalkanone ternary complex decomposes by slow oxidation to the α-ketone followed by fast oxidation to the dione[82].

Recently Dhillon *et al.*[83] oxidized organoboranes by PCC to corresponding aldehydes and ketones. The oxidation of inorganic reductants like As(III)[84], Te(IV)[85] and Tl(I)[86] with PCC in HCl have also been reported.

Oxidation of phosphite[87] and hypophosphite[88] by PCC proceed with the formation of a complex which decomposes in a slow step to generate Cr(IV) followed by its disproportionation.

Recent studies on oxidation of some primary and secondary alcohols[89] *viz.*, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol and 2-methyl butanol in water-perchloric acid medium and hydroxy acids[90] *viz.*, lactic acid and mandelic acid in acidic medium by PCC to the corresponding carbonyl compound and oxoacid, respectively is first order each in [PCC], [substrate] and [H^+]. A mechanism in which water acts as a proton abstracting agent in the rate determining step has been suggested.

Oxidation kinetics of N, α-diphenylnitrones and some *meta* and *para*-substituated N, α-diphenylnitrones with PCC in aqueous DMF medium have been reported recently[91]. The electron releasing substituents accelerate and electron withdrawing substituents retard the oxidation rate.

Oxidation kinetics with pyridinium fluorochromate (PFC): Pyridinium fluorochromate (PFC) has proved to be one of the most reactive species. The reagent was introduced as an oxidizing agent by Bhattacharjee *et al.*[15] and has been widely in use[92-96] since then. Pyridinium fluorochromate in CH_2Cl_2 readily oxidizes primary, secondary and allylic alcohols to the corresponding carbonyls, benzoin to benzil, anthracene and phenanthrene to anthraquinone and phenanthrene-9,10-quinone and triphenylphosphine to triphenylphosphine oxide[93].

In order to throw light on the mechanism of PFC oxidation, it was shown that like PCC, PFC also is a two electron oxidant and the end product is a Cr(IV) species[93].

The oxidation of diols[97], Co(III) bound and unbound α-hydroxy acids[98] (mandelic acid and lactic acid), aromatic acetals[99] and carbonyl compounds from oximes[100] by PFC presented almost similar kinetics to that observed in the oxidation of these substrate by PCC.

The oxidation of alcohols[101-103], α-hydroxy acids[104,105], lower oxyacids of phosphorus[95] benzaldehyde[96], substituted benzaldehydes[106], aliphatic aldehydes[107], oxalic acid and formic acid[108] and thioacid[109] by PFC exhibited Michalies-Menten type kinetics with respect to reductant.

The kinetics of oxidation of secondary alcohols[110,111] and aliphatic secondary alcohol and 1-phenyl ethanol benzhydrol[112], phenols[113] benzaldoxime[114] and salicylaldehyde[115] by PFC have also been investigated.

The product analysis in the oxidation of acetophenone oxime and its *para*-substituted derivative by PFC indicated that the reaction is oxidative hydrolysis[116].

In the oxidation of naphthols[117] and substituted phenols[118] by PFC in glacial acetic acid as solvent, the overall order of oxidation is two and individual order is one in each reactant. An increase in solvent polarity increases the reaction rate.

The oxidation of phenyl methyl sulfides (PMS), phenyl alkyl and diphenyl sulfides by PFC, in DMSO as solvent, has been studied. A mechanism involving a rate-determining electrophilic oxygen transfer from PFC to sulfide has been proposed[119].

The oxidation of some benzyl ether by PFC in glacial acetic acid, in the presence of H_2SO_4, was first order reaction in each PFC, the ether and hydrogen ions. A direct hydride ion transfer mechanism has been suggested[120].

Oxidation of diphenylmethane and fluorene by PFC in aqeous acetic acid containing perchloric acid follows the rate law[121]:

$$-\frac{d[PFC]}{dt} = \frac{Kk_2[PFC][Substrate]}{1+K[Substrate]}$$

The oxidation kinetics of toluene and substituted toluenes by PFC has been studied. A mechanism involving a resonance hybrid as an intermediate has been proposed[122].

Kinetic studies on oxidation of acetophenone and *para* substituted semicarbazones[123] substituted 3,5-dimethyl-2,6-diaryl piperidin-4-one oximes[124], substituted 1-methyl-2,6-diphenyl- piperidin-4-one oximes[125], 2,6-diphenyl-piperidin-4-one semicarbazone and some alkyl substituted 2,6-diphenyl-piperidin-4-one semicarbazones[126] and β-benzoylpropionic acid and *para* substituted β-benzoylpropionic acids[127] by PFC in aqueous acetic acid have also been reported.

The PFC oxidation of D-glucose and some other monosaccharides in aqueous perchloric acid solution, has been reported. A mechanism involving hydride ion transfer is proposed[128].

It is presumed that the oxidation of piperidones by PFC involves the ketone directly rather than the enolic form because PMR study indicates the absence of olefinic proton[129]. Steric effects on the PFC oxidation of some substituted piperidin-4-ones have also been investigated[130,131].

The oxidation of some *ortho*-substituted N, α-di-Ph nitrones[132] and N, α-di-Ph nitrones and some *meta* and *para* substituted N, α-di-Ph nitrones[133] with PFC in aqeous DMF have also been carried out. Attempts have been made to correlate structure with reactivity in the oxidation of substituted anils by PFC[134]. The oxidation of maleic acid, fumaric acid, crotonic

acid and cinnamic acid[135] in DMSO leads to the formation of corresponding epoxide similar to the oxidation of these acids by PCC.

The kinetics and mechanism of the oxidation of cyclohexanone, cyclopentanone, cyclooctanone and various α-substituted cyclohexanones by PFC have been studied. The relative reactivity of various cyclic ketones have been rationalized on the basis of conformational differences and steric factors[136]. The oxidation of alicyclic oximes of cyclopentanone, cyclohexanone and cycloheptanone[137] by PFC follows first order kinetics each in [PFC] and [oxime]. The reactivity sequence observed is cyclohexanone oxime > cyclopentanone oxime > cycloheptanoneoxime which have been rationalized from I-strain.

Oxidation kinetics with pyridinium bromochromate (PBC): Pyridinium bromochromate (PBC) is another mild and selective oxidizing agent used in synthetic organic chemistry[116]. Only reports about the kinetics and mechanism of oxidation of alcohols[138-140], diols[141], α-hydroxy acid[142] (substituted mandelic acid) oxyacids of phosphorus[143], sulfides[144], methionine[145], aliphatic aldehyde[146] oxalic acid and formic acid[147] and thio acid[148], 2-nitrobenzaldehyde[149], α-amino acids[150], glycine[151], tyrosine[152], L-cystine[153], aldo- and keto-oximes[154], unsaturated acids[155] (*viz.* maleic acid, fumaric acid, crotonic acid and cinnamic acid), histidine[156] and *para* and *meta*-substituted cinnamic acids[157] by PBC are available in literature.

Oxidation kinetics with quinolinium halochromate

Oxidation kinetics with quinolinium fluorochromate (QFC): The synthetic potential of quinolinium fluorochromate (QFC) was first reported by Murugesan *et al.*[21] Quinolinium fluorochromate is relatively more soluble in organic solvents than PCC and has more controlled acidity than PFC or PCC. Chaudhuri *et al.*[158] highlighted the versatile nature of QFC as an oxidant reacting with diverse kinds of organic substrates. As far as the reactions with common substrates such as *n*-butanol, benzyl alcohol, *iso*propanol, cyclohexanol, benzoin, triphenylphosphine and allyl alcohol are concenered, the reactions were identical for both the reagents (QFC and PFC) with respect to the reaction times and yields of the oxidized product. Significantly the oxidation of anthracene and phenanthrene was very facile even in CH_2Cl_2 medium[159]. Apart from these, QFC also oxidizes diphenyl sulphide to corresponding sulphoxide in high yields. Besides these, the capability of QFC to act as an oxidizing agent in sensitive environments has been demonstrated by the facile oxidation of secondary hydroxyl group in an environments of *iso*propylidene functionality to the corresponding ketone[159]. Recently, Chandrasekhar *et al.*[160] reported that QFC in dichloromethane is able to deprotect and oxidize the primary alcoholic group, while leaving the protected secondary alcoholic group intact.

The kinetics of oxidation of substituted benzyl alcohol[161], substituted benzaldehydes[162], thiodiglycollic acid[163], allyl alcohol[164], crotonaldehyde[165] and organic sulphides[166] by QFC in aqueous acetic acid have been studied.

The oxidation of aliphatic alcohols[167], diols[168], thioacids[169], α-hydroxy acids[170] (glycollic acid, lactic acid, malic acid and substituted mandelic acid) lower oxyacids of phosphrous[171] and oxalic acid and formic acid[172] and DL methionine[173] by QFC in DMSO, has been studied kinetically. The oxidation of α-hydroxy acids exhibited a first order dependence with respect to each the oxidant and the α-hydroxy acid. The other reactions showed a Michaelis-Menten type kinetics with respect to the reductants.

Oxidation of aliphatic aldehyde by QFC proceeds by a mechanism involving transfer of hydride ion from the aldehyde to the oxidant *via* an intermediate complex[174].

The kinetics of oxidation of phenoxy acetic acids by QFC in binary solvent mixtures indicated that in both solvent system there exists an equilibrium prior to the rate determining step followed by the irreversible decomposition of the complex[175].

Kinetics and mechanism of oxidation of α-hydroxy acids (mandelic acid, lactic acid and glycollic acid) by QFC, in perchloric acid medium have been studied. A mechanism involving the formation of an intermediate between protonated oxidant and substrate which decomposes in a slow step, is proposed[176].

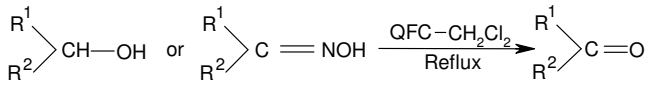
Oxidation of some *ortho*-substituted phenyl methyl suphides with QFC in acetonitrile medium gave sulphone as the oxidation product[177].

The oxidation kinetics of di-Ph, dialkyl and MePh sulphides with QFC have been investigated in MeCN[178].

Kinetic studies on the oxidation of atrolactic acid gave the following rate equation[179]:

$$\text{Rate} = \frac{k_2 K_1 [S][QFC][H^+]}{1 + K_1 [H^+]}$$

Oxidative transformation of alcohols and oximes to carbonyl compounds by QFC is also reported[180].



Enhanced reactivity in the QFC co-oxidation of some cycloalkanones and oxalic acid have been reported recently. π-Complex formation has been envisaged to explain the oxidation of cycloalkanes. The formation of 2:1 oxalic acid-QFC complex has been assumed to be the slow rate limiting step in the oxalic acid-QFC oxidation system. The order of reactivity $C_6 > C_8 > C_5 > C_7$ is explained[181].

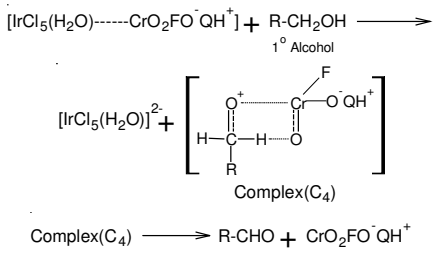
Kinetic investigations on the oxidation of benzylic acid with QFC in aqueous acetic acid exhibits first order dependence with respect to [oxidant] and Michaelis-Menten type kinetics with respect to [substrate]. Decomposition of the cyclic complex formed between the oxidant and substrate is assumed to be the slow and rate determining step[182].

Oxidation of substituted styryl ketones by QFC in aq. acetic acid media in presence of 1,10-phenanthroline lead to the formation of epoxide[183].

Recently Ir (III) catalyzed oxidation of primary alcohols in aqueous perchloric acid medium have been reported[184]. The reaction become facile in the presence of micro-quantity of Ir (III) (10^{-6} M). The following reaction mechanism has been suggested:

$$\underset{C_1}{[IrCl_6]^{3-}} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[IrCl_5(H_2O)]^{2-}} + Cl^- \quad (1)$$

$$[IrCl_5(H_2O)]^{2-} + CrO_2FO^-QH^+ \overset{k_2}{\underset{\text{slow \& r.d.s.}}{\rightleftharpoons}} \underset{\text{Complex}(C_3)}{[IrCl_5(H_2O)\text{------}CrO_2FO^-QH^+]} \quad (2)$$



The rate law for the suggested mechanism is

$$\text{Rate} = \frac{K_1K_2[QFC][Ir(III)]_T}{K_1 + [Cl^-]}$$

Oxidation kinetics with quinolinium bromochromate (QBC): Quinolinium bromochromate (QBC) has been used as a selective and efficient reagent for oxidizing primary and secondary alcohols to the corresponding carbonyl compounds in anhydrous acetic acid medium at room temperature (28-30 ºC) without involving any side reaction as indicated by the following scheme[22]:

Kinetics of oxidation of aliphatic primary alcohols[185], secondary alcohols[186], *vicinal* and *geminal* diols[187], substituted benzyl alcohols[188], aliphatic aldehydes[189], aliphatic aldehydes[190], α-hydroxy acids[191], unsaturated acids[192], lower oxyacids of phosphorus[193], thio acids[194], organic sulphides[195], aldo- and keto-oximes[196], DL-methionine[197], formic acid and oxalic acid[198] by QBC using DMSO as solvent have been studied. The reactions exhibit first order dependence on both the oxidant and reductant[185-198], except the oxidation reactions of formic acid and oxalic acid where Michaelis-Menten type kinetic with respect to reductants were obtained. In the oxidation by QBC, mechanism involving transfer of hydride ion[186,188-191], symmetrical transition state[187,198], formation of thioester[194], three certre transition state[192], formation of sulfurane intermediate[195], formation of cyclic intermediate[196] has been suggested. Oxidation of benzaldehyde, *p*-nitro and *m*-nitrobenzaldehydes[199,200] and *p*-substituted benzaldehydes[201] by QBC in aqueous acetic acid medium leading to the formation of corresponding benzoic acid and Cr(III) is first order in QBC, benzaldehyde and second order with respect to [H^+]. Formation of chromic ester between hydrated benzaldehyde and prontonated QBC followed by C-H bond fission in slow step explain the observed experimental facts.

Oxidation kinetics with quinolinium chlorochromate (QCC): The synthetic and kinetic aspects of redox reactions of quinolinium chlorochromate (QCC) with organic substrates have already been reviewed[202]. Therefore, the studies reported thereafter are included in this review.

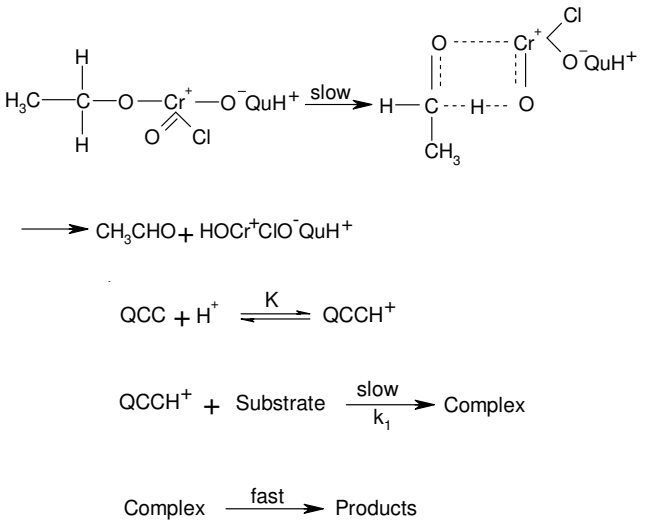
Recently Elango *et al.* have reported solvents and structural effects on the oxidation kinetics of benzaldehyde[203], substituted benzaldehydes[204], 2,6-diphenyl piperidin-4-ones[205], 3-R-2,6-diphenyl piperidin-4-ones[206] with QCC. The rate data have been correlated with different solvent parameters using multiple regression analysis.

The kinetics of oxidation of some reducing sugars[207-212] with QCC in acetic acid medium have been studied at constant ionic strength. The reactions are of first order each in [oxidant] and [sugar]. The experimental results have been assumed in terms of mechanism involving transfer of hydride ion similar to PCC oxidation of reducing sugars[213,214].

The kinetics of oxidation of some unsaturated organic substrates[215-219] by QCC investigated in 50 % acetic acid-50 % water mixture follows the following rate law:

$$-\frac{d[QCC]}{dt} = k_{obs}[QCC][substrate][H^+]$$

The protonated form of the oxidant are found to be more efficient in acidic medium similar to PCC[220] and QFC oxidation[164,165]. A mechanism involving the transfer of oxygen from oxidant to the substrate has been suggested (**Scheme-I**).



The oxidation of methionine by QCC in presence of chloroacetic acid and in water-acetic acid mixture of varying mole fractions shows that the reaction is first order with respect to methionine, QCC and acid[221].

The kinetics and mechanism of the oxidation of aldonitrones (nitrone) by QFC in aq. DMF in the absence and presence of oxalic acid have been reported[222]. The reaction is first order each with respect to the concentration of nitrone, QCC and oxalic acid and fractional order with respect to H^+ concentration. Oxalic acid acts only as a catalyst. A mechanism involving protonated nitrone and QCC as the reactive oxidant is proposed.

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