

## REVIEW

**Quinolinium Chlorochromate: A Novel Oxidant, Kinetic and Synthetic Aspects**

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A number of newer oxochromium(VI) reagents have been introduced recently as oxidising agents for the oxidation of organic substrates. Quinolinium chlorochromate adds to the select list as the most significant recent chromium(VI) oxidant for the effective and selective oxidation of organic substrates under mild conditions. This review highlights the recent work on the kinetics and mechanism of the reactions of organic substrates using this oxidant. Some of the novel synthetic uses of this reagent are also discussed.

## INTRODUCTION

Chromium oxidation has been widely explored since the very beginning of organic chemistry, and the topic remains of current interest because of the development of newer oxochromium(VI) reagent for the effective and selective oxidation of organic substrates under mild conditions<sup>1-8</sup>. A useful class of such reagent is quinolinium chlorochromate (QCC)<sup>9</sup> which is being successfully used in the area of oxidation in organic chemistry<sup>10, 11</sup>. It has also received sufficient attention as a novel compound in organic synthesis. This review highlights the recent work on the kinetics and mechanism of the reactions of this compound. Some of the novel synthetic uses of this reagent are also described.

Quinolinium chlorochromate<sup>9</sup>,  $C_9H_7N^+HClCrO_3^-$ , a stable reagent originally introduced as an oxidising agent for alcohols<sup>10, 11</sup> is used in synthetic organic chemistry. QCC is simpler to prepare and is not air or moisture sensitive. Oxidation with it does not involve handling a large volume of solvent and well suited for moderate to large scale oxidation.

**Oxidation stability:** Quinolinium chlorochromate is quite stable. It is not appreciably hygroscopic and has excellent shelf life as no deterioration in its oxidation ability was observed even after a few months of storage at ambient temperature. It is soluble in water, dimethyl formamide and dimethyl sulfoxide; sparingly soluble in methylene chloride and chloroform and insoluble in ether, ethyl acetate, toluene, heptane. The structure of QCC (m.w. = 265.62, m.p. 65°C) has been confirmed by elemental analysis.<sup>10, 11</sup>

**Standardisation of QCC:** A solution of QCC can be standardised by

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titrimetric procedure. Aliquots of the solution prepared in required solvent are pipetted out into an iodine-flask containing 10 mL of 10% KI solution. The liberated iodine is titrated against standard sodium thiosulphate solution to a starch end point.

**Preparation of quinolinium chlorochromate:** Quinolinium chlorochromate can be easily and safely prepared by the careful addition of quinoline to a solution of chromium trioxide in 6 M hydrochloric acid over 10 min. The yellow-orange solid precipitates out and is collected on a sintered glass funnel and dried for 1 h in vacuum. The yellow orange reagent can be stored in brown bottles. It can be used as such without purification.

**Synthetic utility of quinolinium chlorochromate:** Quinolinium chlorochromate is an efficient reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively<sup>10</sup>. This reagent works as efficiently as activated manganese dioxide<sup>12</sup> or Collins reagent<sup>13</sup>. Some typical results for the oxidation of alcohols are summarised in Table-1.

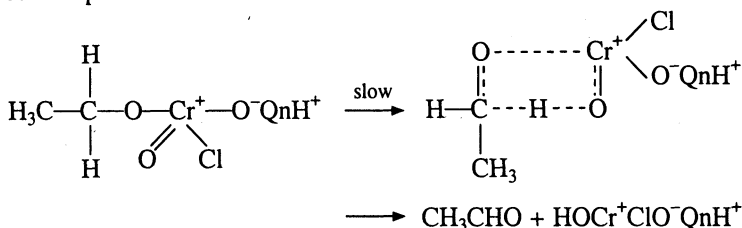
TABLE-1  
PRODUCTS OF OXIDATION OF PRIMARY AND SECONDARY  
ALCOHOLS WITH QCC

Alcohol	Product	Yield (%)	
		(QCC in CH <sub>2</sub> Cl <sub>2</sub> )	(QCC in DMF)
<i>n</i> -Butanol	<i>n</i> -Butanal	72	58
<i>n</i> -Hexanol	<i>n</i> -Hexanal	71	52
<i>n</i> -Heptanol	<i>n</i> -Heptanal	59	48
<i>n</i> -Octanol	<i>n</i> -Octanal	58	46
Cyclohexanol	Cyclohexanone	66	52
1-Bromopentanol	1-Bromopentanal	56	—
Benzyl alcohol	Benzaldehyde	82	49
Benzhydrol	Benzophenone	79	58
Benzoin	Benzil	82	67

Quinolinium chlorochromate behaves very much like pyridinium chlorochromate (PCC)<sup>2</sup> and possesses excellent selectivity to oxidise primary alcohol in the presence of secondary alcohol under normal reaction conditions<sup>11</sup>. It oxidises primary alcohol to the corresponding aldehydes in a reaction time of 1–2 h while it takes around 12 h for the oxidation of secondary alcohols. This happens irrespective of the fact whether both hydroxyl groups are present in the same molecule or are present in different molecules. This difference in the rate of oxidation is envisaged due to steric factors. The detailed mechanism of oxidation is complex and is perhaps not very clear. It has, however, been reported<sup>14</sup> that after the chromate ester formation the abstraction of hydrogen is intermolecular and there is a steric interaction between the peri-hydrogen of quinoline and the group present on C (may be H or R) other than the H which has to be abstracted as depicted in chart I.



a cyclic hydride transfer takes place. Based on these facts the mechanism proposed is presented in Scheme-1.

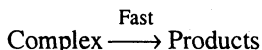
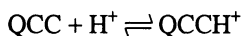


SCHEME-1

The kinetics of oxidation of some  $\alpha$ -hydroxy acids<sup>16</sup> (mandelic, lactic and glycolic acid) in aqueous medium showed first order kinetics with respect to oxidant and fractional order with respect to substrate.

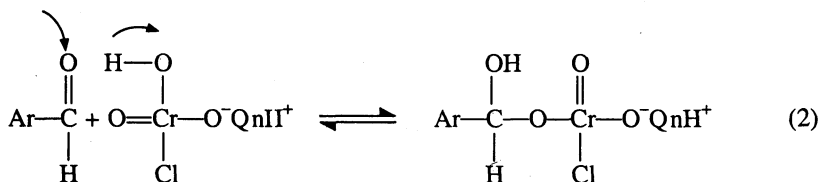
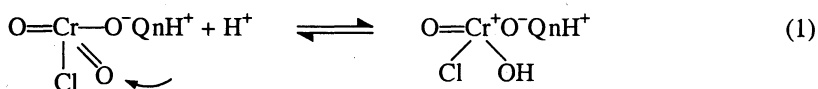
A comparative kinetic study of phenoxyacetic acid by quinolinium fluorochromate (QFC) and quinolinium chlorochromate (QCC) was carried out by Karthikeyan *et al.*<sup>17</sup> They showed that the reactivity of QCC was less than QFC and suggested a polar rate limiting transition state.

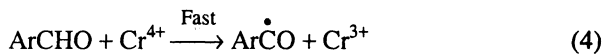
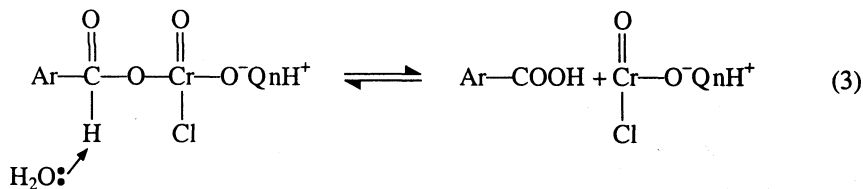
QCC oxidises thiodiglycolic acid<sup>18</sup> to sulphonyldiacetic acid in aquo acetic acid media and follows a unit dependence both in oxidant and substrate. The probable mechanism involves the attack of the protonated oxidant to the substrate to form a complex in a rate determining step as given in the following scheme.



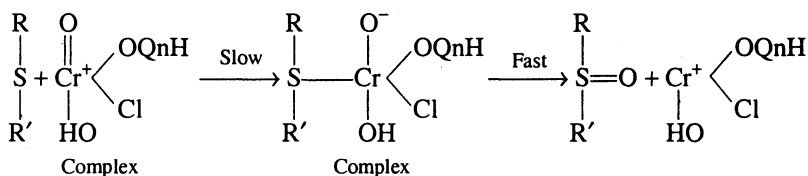
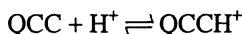
The oxidation kinetics of substituted benzyl alcohols by QCC involves decomposition of an initially formed chromate ester *via* a concerted symmetrical transition state<sup>19</sup>.

The kinetics of oxidation of benzaldehyde and several *para*- and *meta*-substituted benzaldehydes to the corresponding benzoic acid have been studied by Jameel<sup>20</sup>. The reaction proceeds with the formation of QCC-ester as the intermediate in the scheme given below:





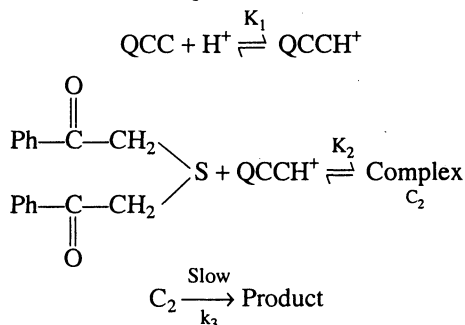
The rate of oxidation of dialkyl and alkyl phenyl sulphides<sup>21</sup> by QCC have been studied in aqueous acetic acid. The proposed mechanism envisages oxygen transfer from QCC which is in agreement with the earlier observations<sup>24-26</sup>



Mechanistic investigations of oxidation of diphenacyl sulphide by QCC in aqueous acetic acid exhibited the following rate equation<sup>22</sup>:

$$k_{\text{obs}} = \frac{K_1 K_2 k_3 [\text{S}][\text{H}^+]}{1 + K_1 [\text{H}^+]}$$

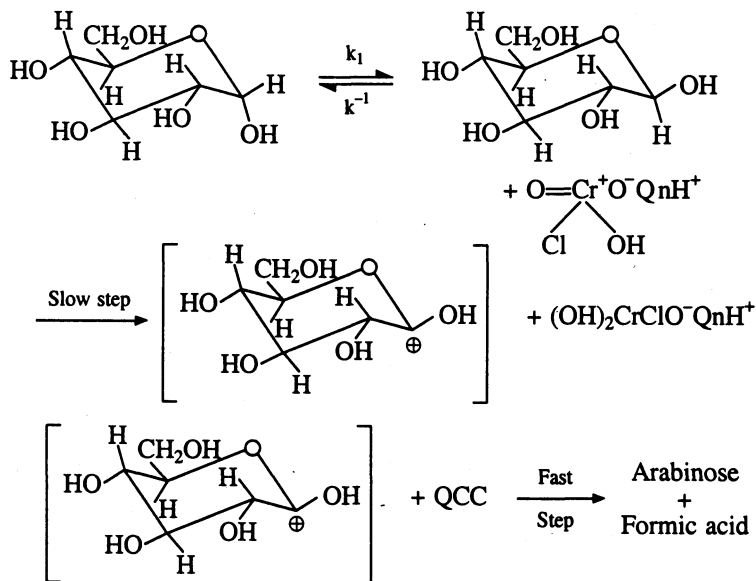
The suggested mechanism involves the protonated form of the oxidant which attacks the substrate to form a complex. The complex decomposes to give diphenacyl sulphoxide in a slow step.



The kinetics and mechanism of oxidation of a number of *meta*- and *para*-substituted aromatic anils by QCC were studied in aq. acetic acid. The reaction

is first order with respect to anil and QCC and second order with respect to hydrogen ions<sup>23</sup>.

The studies of the kinetics of oxidation of reducing sugar which contain a large number of functional groups unlike most organic substrates and in which the functional groups and competing reactions frequently occur are of particular interest. The kinetics of oxidation of D-glucose<sup>27</sup> with QCC in acetic acid medium have been studied at constant ionic strength. The reaction is of first order each in [oxidant] and [D-glucose]. Arabinose and formic acid have been identified as the main products of the reaction. The experimental results can be accounted in terms of mechanism involving hydride ion transfer as envisaged in Scheme-I.

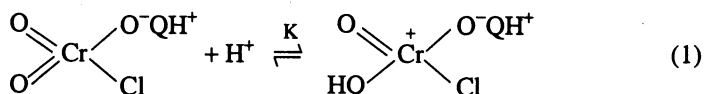


Scheme-I

The kinetics of epoxidation of allyl alcohol<sup>28</sup> by QCC investigated in 50% acetic acid and 50% water mixture, follows the following rate law:

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

The protonated forms of the oxidant are found to be more effective in acid medium similar to pyridinium chlorochromate (PCC)<sup>29</sup> and quinolinium fluorchromate (QFC)<sup>30</sup> oxidation. The reaction proceeds with either scheme I or II.





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