

TETRAETHYLAMMONIUM CHLOROCHROMATE : A NOVEL OXIDANT, KINETIC AND MECHANISTIC ASPECT

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Organic halochromates, a new class of mild Cr(VI) reagents have been introduced recently as oxidising agents for the oxidation of organic substrates owing to their being versatile, operationally simple, and easily accessible. These reagents have been found to be better in their reactivity and selectivity compared to common Cr(VI) oxidant. Tetraethylammonium chlorochromate adds to the select list of newer Cr(VI) reagents as the most significant 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.

INTRODUCTION

The development of newer Cr(VI) reagents for the effective and selective oxidation of organic substrates under mild conditions has been going on because Cr (VI) is a versatile oxidant for the oxidation of many types of organic substrates and also due to the advancement in the synthesis of complex organic molecules under different reaction conditions [1-3]. Tetraethylammonium chlorochromate (TEACC) is one of such useful Cr (VI) reagent which is being successfully used in the area of oxidation in organic chemistry [4]. 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.

Tetraethylammonium chlorochromate, $C_8H_{20}N^+CrO_3Cl$, is a stable reagent originally introduced as an oxidising agent for benzyl alcohol [4]. It is now used in synthetic organic chemistry. It is easier to prepare and is not air or moisture sensitive. Oxidation with it does not involve a large volume of solvent and well suited for moderate to large scale oxidation.

Oxidation Stability

Tetraethylammonium chlorochromate is quite stable, soluble in water and in many organic solvents and convenient to use. 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. The structure [5] of TEACC (m.w. = 265.699, m.p. 225-26°C, pH = 2.15 at 30°C) has been characterized by elemental analysis, IR, UV/Visible, 1H -NMR and ^{13}C -NMR techniques and single X-ray diffraction analysis (monoclinic system, space group C2 (#5), with $a = 12.023$ (3), $b = 7.998$ (2), $c = 14.527$ (4) Å, $\beta = 114.187$ (4)°, $V = 1274.4$ (6) Å³ and $Z = 4$). X-ray data determined the CH---O hydrogen bond that forms between the ethyl hydrogen of the cation and oxygen of the anion due to which there is inequality between the Cr—O and Cr—Cl bond length that is responsible for the higher reactivity of this compound over similar oxidising agent in terms of the amount of oxidant and solvent required, short reaction times and high yields.

Standardisation of TEACC:

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

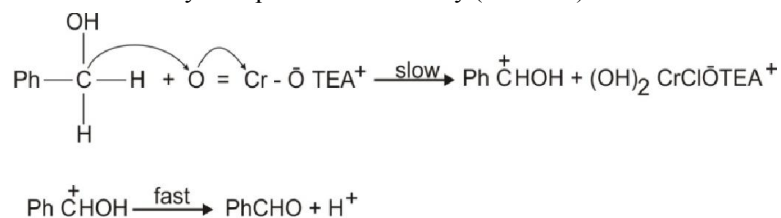
Preparation of tetraethylammonium chlorochromate:

Tetraethylammonium chlorochromate can be easily and safely prepared by the careful addition of tetraethylammonium hydroxide (20% in H₂O) to a solution of chromium trioxide in 6M hydrochloric acid over 10 min. The orange-yellow solid precipitates out and is collected on a glass funnel. It was washed and dried under reduced pressure for 3h. The orange-yellow reagent can be stored in brown bottles. It can be used as such without purification.

Kinetic and Mechanistic Aspects of Oxidations by Tetraethylammonium Chlorochromate

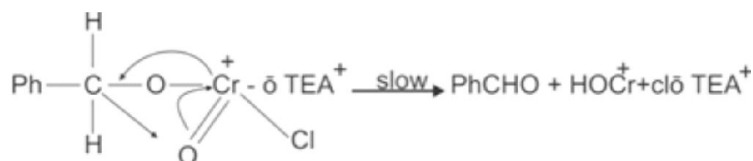
Studies have been made on the kinetics and mechanism of the oxidation of benzyl alcohol [4], α -hydroxy acid [6] (glycolic, lactic, malic and a few substituted mandelic acids), lower oxyacids of phosphorus [7], diols and their monoethers [8], organic sulfides [9] aliphatic primary alcohol [10], aliphatic aldehydes [11], monosubstituted benzaldehydes [12], aldo- and keto-oximes [13], methionine [14], oxalic and formic acid [15], unsaturated acids [16] (maleic, fumaric, crotonic and cinnamic acids), DL-methionine [17], aliphatic secondary alcohols [18], aldo- and keto-hexoses [19-23] (D-glucose, D-mannose, D-galactose, D-fructose and L-sorbose) and unsaturated organic substrates [24-28] (crotonaldehyde, crotyl alcohol, allyl alcohol, acrylic acid and maleic acid) by TEACC.

First of all Murugensan *et al* [4]. synthesized TEACC and reported the kinetics of oxidation of benzyl alcohol by this reagent in dimethylformamide (DMF). The oxidation reaction was found first order with respect to both TEACC and alcohol. The reaction was catalysed by acid, and showed a first order dependence on [acid]. The linear increase in the oxidation rate of alcohol with acidity suggests the involvement of protonated Cr (VI) species in the rate determining step which is confirmed by the decrease in the rate of oxidation with an increase in dielectric constant of the medium. The reaction does not induce the polymerisation of acrylonitrile. As a result one-electron oxidation was quite unlikely. The observed kinetic results indicated hydride ion transfer in the rate-determining step of the oxidation reaction. The hydride ion transfer may take place either directly (scheme 1)



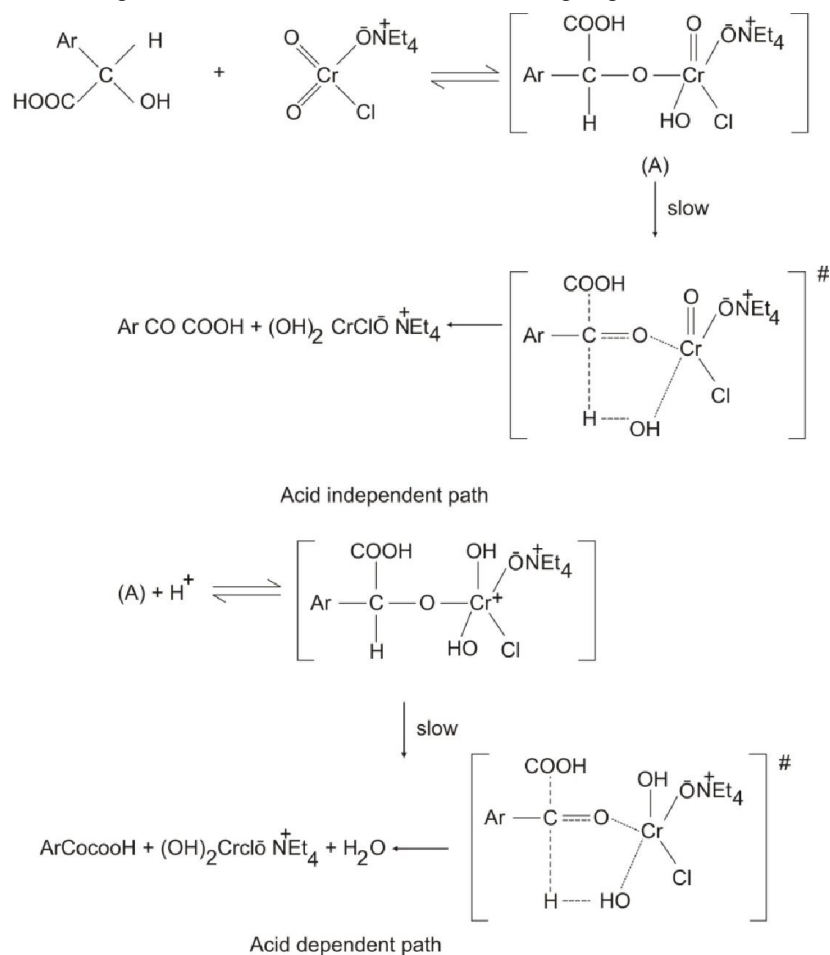
Scheme 1

or may involve the prior formation of chromate ester (scheme 2).



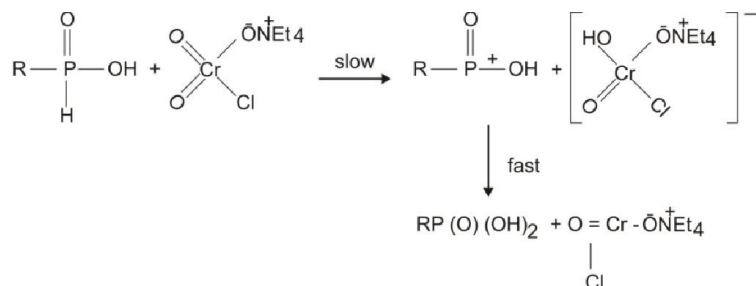
Scheme 2

The kinetics of oxidation of some α -hydroxy acids [6] (glycolic, lactic, malic and a few substituted mandelic acids) by TEACC have been studied in dimethylsulfoxide (DMSO). The rate shows first order dependence each on [TEACC] and [acid]. The reaction is catalysed by hydrogen ions. Two mechanistic pathways for acid independent and acid dependent reactions have been suggested (Scheme 3). The acid catalysis was attributed to the protonation of TEACC to give a stronger oxidant and electrophile. The oxidation of α -deuteriomandelic acid showed the presence of a primary kinetic isotope effect ($k_H/k_D = 5.63$ at 298 K), which suggests the cleavage of the C-H bond in the rate-determining step.



Scheme 3

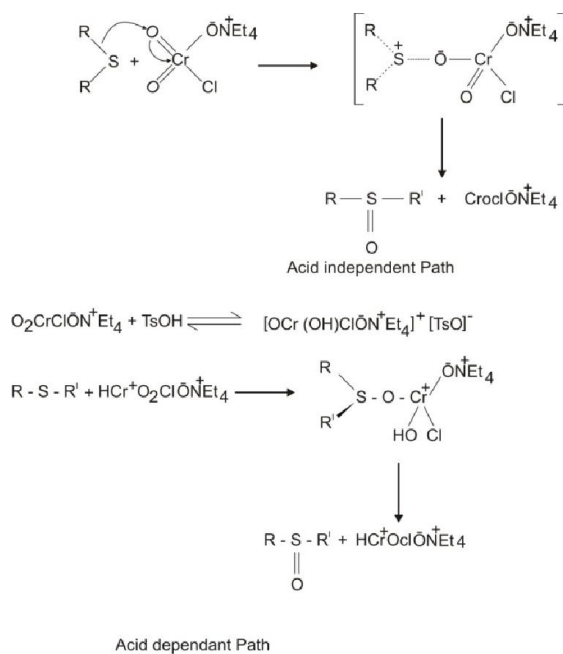
Oxidation of some lower oxyacids of phosphorus by TEACC in DMSO leads to the formation of corresponding oxyacids with phosphorus in a higher oxidation state [7]. The reaction is first order each with respect to TEACC and oxyacids. The presence of a substantial kinetic isotope effect confirms the cleavage of a P-H bond in the rate determining step. A mechanism involving transfer of a hydride ion in the rate determining step has been proposed (Scheme 4)



Scheme 4

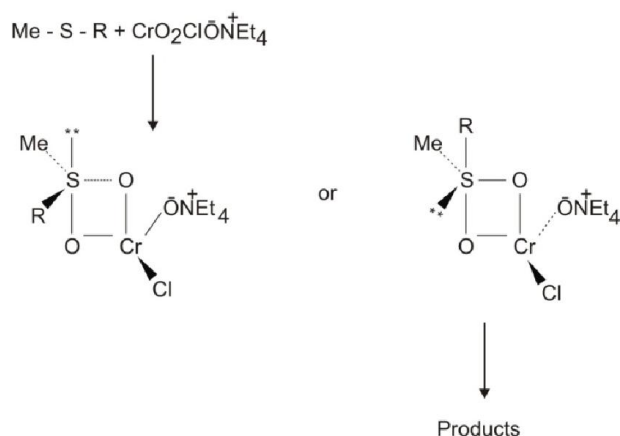
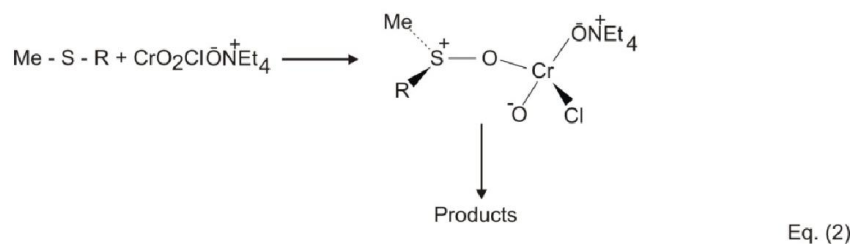
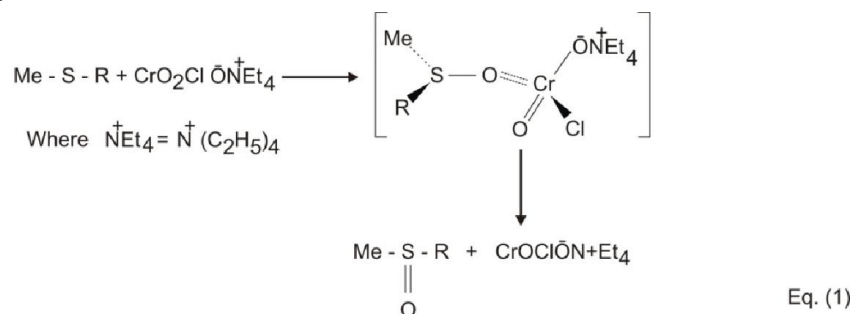
Kinetics of oxidation of some vicinal and non vicinal diols and their monoethers to corresponding hydroxycarbonyl compound by TEACC in DMSO was found first order in TEACC and diols [8]. The temperature dependence of the kinetic isotope effect indicated the presence of a symmetrical transition state in rate-determining step.

The toluene-p-sulfonic acid (TsOH) catalysed oxidation of organic sulfides [9] to corresponding sulfoxides by TEACC was first order with respect to both TEACC and sulfide. Two mechanistic pathways, one TsOH-catalysed and the other uncatalysed have been suggested. The contribution of steric constants are in agreement with the acyclic mechanism that involves the rate determining electrophilic oxygen transfer from TEACC to the sulfide (Scheme 5).



Scheme 5

TEACC oxidises aliphatic primary alcohol [10] to corresponding aldehydes and aliphatic aldehydes [11] to corresponding carboxylic acids in DMSO and follows a unit dependence both in [oxidant] and [substrate]. A mechanism involving transfer of hydride ion has been suggested.



Scheme 6

Eq. (3)

The oxidation kinetics of monosubstituted benzaldehydes with TEACC in DMSO is first order with respect to both TEACC and aldehydes. The reaction is promoted by hydrogen ions. The oxidation of deuterated benzaldehydes exhibits a substantial primary kinetic isotope effect. Based on linear regression analysis it was observed that the oxidation of para-substituted benzaldehydes is more susceptible to the delocalised effect than that of ortho- and meta-substituted ones, which display a greater dependence on the field effect. The presence of an electron deficient reaction centre in the rate-determining step has been suggested.

The oxidative deoxygenation of several aldo- and keto-oximes by TEACC in DMSO, exhibited a first order dependence on both the oxime and TEACC. The oxidation of ketoximes was slower than that of aldoximes [13]. A mechanism involving the formation of a cyclic intermediate in the rate-determining step was proposed. The slower oxidation rate for ketoximes was attributed to the steric hindrance by the alkyl groups.

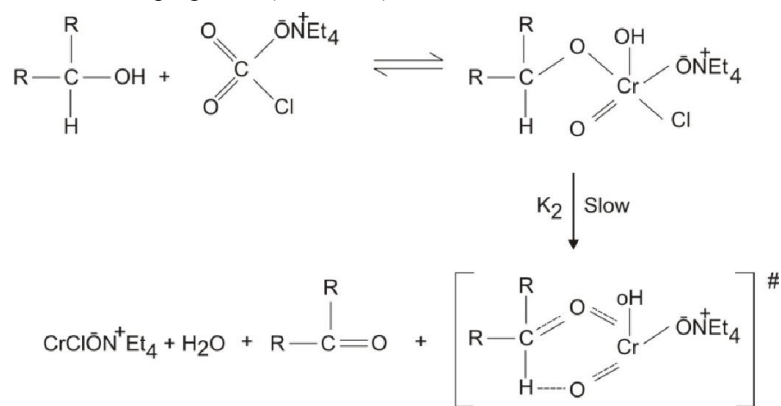
Kinetics and mechanism of oxidation of methionine [14] by TEACC in DMSO leading to the formation of corresponding sulfoxide have been reported recently. The reaction is first order each in methionine and TEACC. The reaction is catalysed by hydrogen ions. The proposed mechanism envisages rate-determining electrophilic oxygen transfer from TEACC to sulfide as shown in Eq. 1 (Scheme 6) which is in agreement with earlier observations [29-30]. The solvent effect supports a transition state depicted in Eq. (1), rather than a sulfonium ion in an S_N2 -like transition state as shown in Eq. (2). The possibility of the formation of a cyclic transition state (Eq. 3) as suggested in many reactions of Cr(VI) [31-32] was also ruled out as it entails a more exacting specificity of orientation and should result in a much larger negative entropy of activation than that observed.

Sharma *et. al* reported the kinetics of oxidation of oxalic and formic acids to carbon dioxide as the main product by using TEACC as the oxidant in DMSO. The reaction is first order with respect to TEACC and the organic acids. The reaction is acid catalysed. The temperature dependence of kinetic isotope effect indicated the presence of a symmetrical cyclic transition state in the rate determining step.

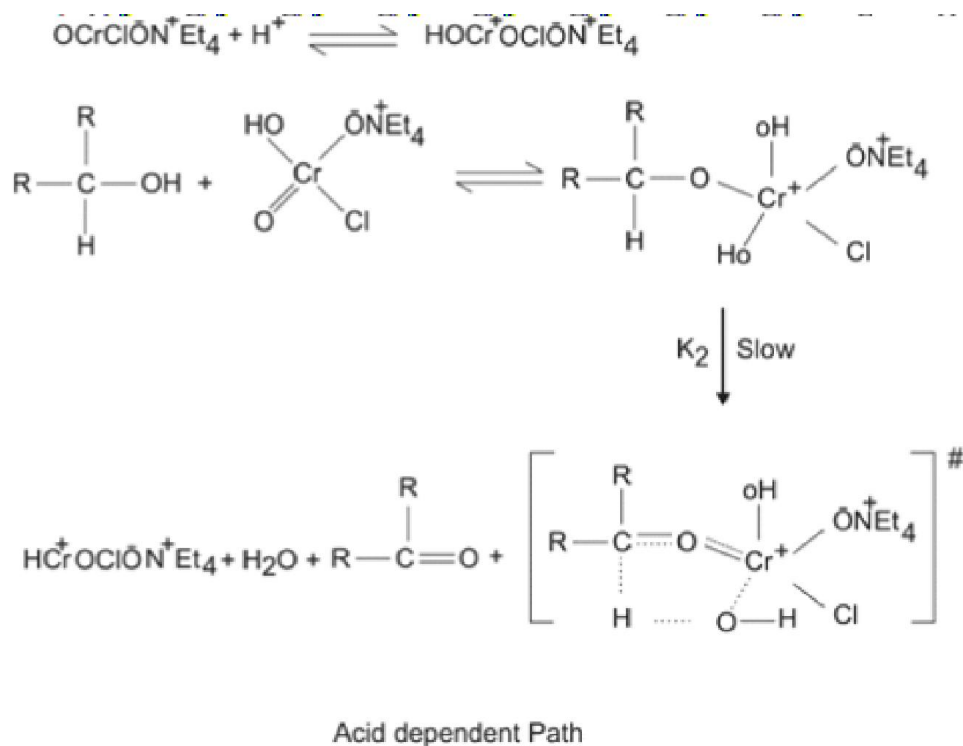
The oxidation of some unsaturated acids [16] (maleic fumaric crotonic and cinnamic acids) by TEACC in DMSO resulting in the formation of corresponding epoxide have been studied. A first order dependency was found with respect to both TEACC and acids. The reaction is catalysed by hydrogen ions. A mechanism involving a three-centre transition state has been postulated.

The oxidation of DL - methionine [17] by TEACC in DMSO to the formation of corresponding sulphoxide is of first order with respect to both TEACC and methionine.

The oxidation kinetics of several aliphatic secondary alcohols [18] to the corresponding ketones in DMSO by TEACC revealed first order kinetics with respect to both oxidant and substrate. A mechanism involving transfer of hydride ion from alcohol to the oxidant, via a chromate ester, has been proposed, (Scheme-7)



Acid independent Path



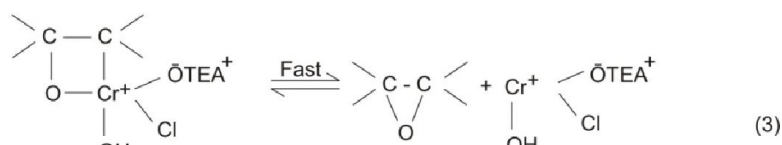
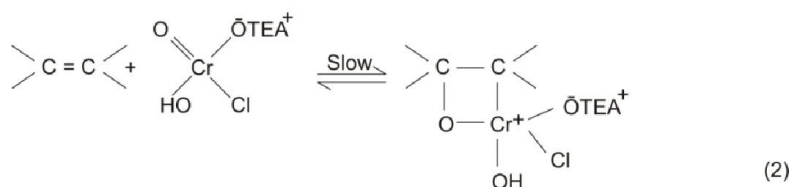
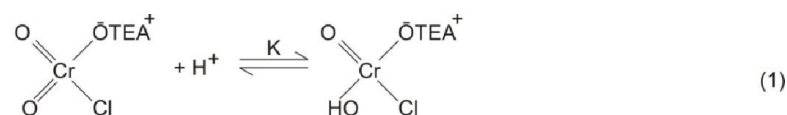
Scheme 7

The kinetics of oxidation of aldohexoses [19-21] (D-glucose [19], D-mannose [20] and D-galactose) [21] and ketohexoses [22, 23] (D-fructose [22] and L-sorbose [23]) with TEACC in acetic acid medium in the presence of perchloric acid have been studied at constant ionic strength. The reaction is first order each in [oxidant] and [substrate]. Arabinose and formic acid have been identified as the oxidation product for D-glucose and D-mannose. In case of D-galactose the oxidation products were D-lyxose and formic acid. The oxidation products identified for D-fructose and L-sorbose were D-erythrose and glycolic acid. Each reaction was catalysed by $[\text{H}^+]$. The experimental results could be accounted in terms of a mechanism involving hydride ion transfer.

The kinetics of epoxidation of some unsaturated organic substrates [24-28], (crotonaldehyde [24], crotyl alcohol [25], allyl alcohol [26], acrylic acid and maleic acid [28]) by TEACC investigated in 50% acetic acid and 50% water mixture follows the following rate Law:

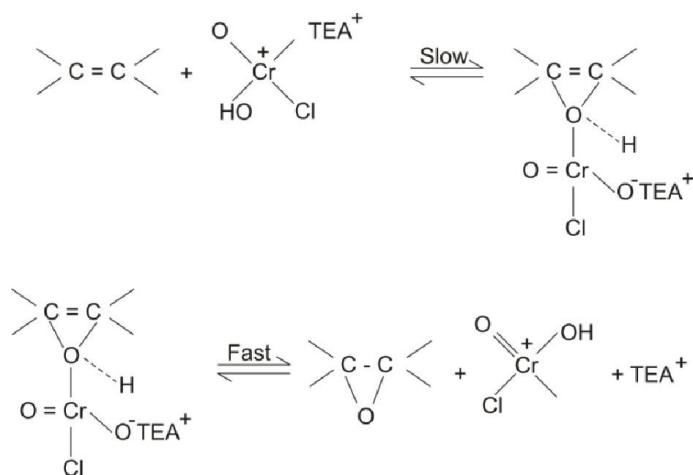
The protonated forms of the oxidant are found to be more effective in acid medium similar to pyridinium chlorochromate (PCC) [33], quinolinium fluorochromate (QFC) [34] and quinolinium chlorochromate (QCC) [35] oxidation. The reaction proceeds with either scheme I or II.

$$-\frac{d}{dt} [\text{TEACC}] = k_{\text{obs}} [\text{TEACC}] [\text{Substrate}] [\text{H}^+]$$



Scheme I

In the proposed mechanism a direct chromium to carbon bond does not account the insensitivity to steric effects very often observed in the addition of olefins [36] by Cr (VI). Thus the most favourable reaction path may be three centered type addition as depicted in scheme II.



Scheme II

Both scheme envisage oxygen transfer from oxidant to the substrate which is in accordance with the earlier observations made for unsaturated organic substrates [37, 38].

CONCLUSION

Tetraethylammonium chlorochromate is described as an efficient reagent for the oxidation of a variety of functional groups under different reaction conditions. The mechanism of its reaction is discussed to a large extent.

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