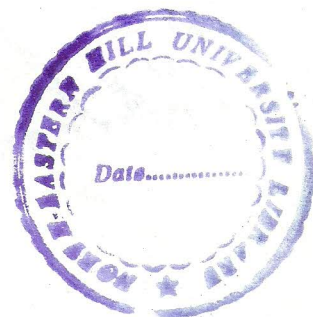


# KINETICS OF OXIDATION OF SOME ORGANIC COMPOUNDS BY QUINOLINIUM DICHROMATE



*BY*

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# The North-Eastern Hill University

## Declaration

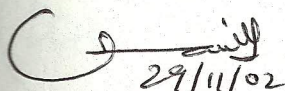
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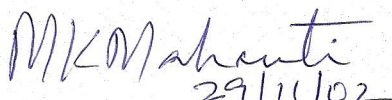
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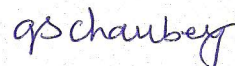
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Place: Shillong

Date: 29/11/02

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## ABSTRACT

Hexavalent chromium compounds have been widely used as oxidizing agents reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to evince keen interest. Over the years, a large number of novel chromium(VI) oxidizing agents have been introduced especially for complex or highly sensitive substrates where great selectivity and effectiveness, coupled with mildness of conditions, are prerequisites for success.

Some of the chromium(VI) reagents which have been used as efficient oxidizing agents have included :

Chromium trioxide; chromyl chloride; Jones reagent – a solution of chromium(VI) oxide in concentrated sulfuric acid (1); Collins reagent – dipyridinium chromium(VI) oxide in dichloromethane (2) ; chromium(VI) oxide adsorbed on solid supports such as graphite, silica, alumina, silica gel, and celite (3,4); Corey's reagent – pyridinium chlorochromate (PCC) in dichloromethane (5); pyridine oxodiperoxochromium(VI) reagent – a complex of chromium pentoxide with pyridine (6); pyridinium dichromate (PDC) used either in solution in dimethylformamide or as a suspension in dichloromethane (7); bis-tetrabutyl ammonium dichromate (TBADC) in refluxing dichloromethane (8); pyridinium fluorochromate in dichloromethane (9); 4-(dimethylamino) pyridinium chlorochromate (10); tetrabutyl ammonium

chlorochromate (TBACC) in chloroform (11); bis-(trimethylsilyl) peroxide (BTSP) in dichloromethane, in the presence of pyridinium dichromate (PDC) (12); pyridinium chlorochromate (PCC) in conjunction with 3,5-dimethyl pyrazole (DMP) in dichloromethane (13,14); chromium(VI) oxide diperoxide (15); diverse chlorochromate reagents such as benzyltrimethyl ammonium chlorochromate (BTMACC), tetrabutyl ammonium chlorochromate (TMACC) in dichloroethane (16); some fluorochromates such as tetramethyl ammonium fluorochromate (TMAFC) and tetrabutyl ammonium fluorochromate (TBAFC) also in dichloroethane (16); tetrakis(pyridine) silver dichromate in refluxing benzene (17); peroxyacetic acid as the stoichiometric oxidant and a catalytic amount of 2,4-dimethylpentane-2,4-diol cyclic chromate in carbon tetrachloride-dichloromethane mixtures (18); chlorotrimethylsilanechromium trioxide (19); benzotriazole in conjunction with pyridinium chlorochromate (PCC) in dichloromethane (20); 2-cyanopyridinium chlorochromate and powdered molecular sieves in dichloromethane (21); 3-carboxy pyridinium dichromate and 4-carboxypyridinium dichromate in pyridine (22); a small quantity of anhydrous acetic acid added to pyridinium dichromate (PDC) and freshly activated molecular sieve powder in dichloromethane (23); chromium peroxide complexes (24); imidazolium dichromate (IDC) in dimethylformamide (25); pyridinium bromochromate (PBC) in chloroform (26); benzyltriethyl ammonium chlorochromate (BTACC) generated, in situ, under phase transfer conditions in refluxing chloroform (27); biphosphonium dichromate reagents (28); zinc-dichromate trihydrate in dichloromethane (29); catalytic amounts of chromium trioxide and an excess of aqueous t-butylhydroperoxide (30); cyanopyridinium chlorochromate (CPCC) in dichloromethane (31); pyridinium

chlorochromate in conjunction with silica gel and by the use of the ultrasound technique (32); pyridinium chlorochromate (PCC) in chloroform, using anhydrous acetic acid as a catalyst (33); 1-methyl imidazolium chlorochromate (MCC) and imidazolium chlorochromate (ICC) in chloroform (34); isoquinolinium chlorochromate in dichloromethane (35); ferric dichromate, polyvinylpyridine supported zinc dichromate, and polyvinylpyridine supported ferric dichromate, taken in acetonitrile (36); chromium trioxide in the presence of wet aluminium oxide taken in hexane (37); and quinolinium fluorochromate (QFC), used in chloroform as solvent (38).

The reagent employed in the present investigation has been quinolinium dichromate (QDC),  $(C_9H_7N^+H)_2Cr_2O_7^{2-}$ . This reagent was first reported to have been used for the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, and for the oxidation of aldehydes to acids (39). This reagent has now emerged as a very useful and versatile oxidant, and has been used for the oxidation of a variety of organic substrates. When taken in dimethylformamide or in dimethylformamide-water mixtures, in the presence of acid, quinolinium dichromate (QDC) was found to be very efficient for the oxidation of benzyl alcohols (40), arylalkanes (41), diphenylamines (42), polynuclear aromatic hydrocarbons (43,44), toluene and substituted toluenes (44,45), fluorene (46), amino acids (47), benzoin (48), styrenes (49), unsaturated acids (50), bicyclic alcohols (51), cyclic alcohols (52), diols (53,54), allylic alcohols (55), primary and secondary alcohols (56,57),  $\alpha$ -hydroxy acids (58, 59), benzyl amines (60), anilines (61), and aromatic and aliphatic ketones (62,63).

The present investigation focuses attention on the kinetic features pertaining to the oxidation of various aldehydes by quinolinium dichromate (QDC) in acid medium, under a nitrogen atmosphere. The rationale governing the present kinetic investigation has been to enlarge the scope of this versatile oxidizing agent, quinolinium dichromate (QDC), in acidic medium, and to provide experimental evidence for the mechanistic pathways of reactions involving diverse organic substrates. The substrates which have been used for the purpose of oxidation by quinolinium dichromate (QDC), in acid medium, using water (in the case of aliphatic aldehydes and dialdehydes), and aqueous acetic acid (in the case of long chain aliphatic aldehydes,  $\alpha,\beta$ -unsaturated aldehydes and heterocyclic aldehydes), have included the following :

1. **Aliphatic Aldehydes - Chapter I**

- I. Acetaldehyde, Propionaldehyde, Butyraldehyde, Valeraldehyde, Isobutyraldehyde and Isovaleraldehyde.
- II. Caproaldehyde, Heptaldehyde, Caprylaldehyde, Pelargonaldehyde and Caprinaldehyde.
- III. Glyoxal and Glutaraldehyde.

2.  **$\alpha, \beta$ -Unsaturated Aldehydes - Chapter II**

Acrylaldehyde, Methacrylaldehyde, Crotonaldehyde, Cinnamaldehyde.

### 3. Heterocyclic Aldehydes - Chapter III

#### I. Five-membered heterocyclic aldehydes :

2-Furaldehyde, 5-Methyl-2-Furaldehyde, 5-Bromo-2-Furaldehyde, 2-Pyrrolecarbaldehyde and 2-Thiophenecarbaldehyde.

#### II. Six-membered heterocyclic aldehydes :

2-Pyridinecarbaldehyde and 3-Pyridinecarbaldehyde.

## Chapter I – Kinetics of Oxidation of Aliphatic Aldehydes

The kinetics of oxidation of aliphatic aldehydes (acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, caprylaldehyde, pelargonaldehyde, caprinaldehyde, isobutyraldehyde, isovaleraldehyde, glutaraldehyde and glyoxal) by quinolinium dichromate (QDC) has been studied in acid medium, using water and water-acetic acid mixtures, as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440 nm. For all the aliphatic aldehydes studied, stoichiometric ratios,  $\Delta[\text{QDC}] / \Delta [\text{substrate}]$ , in the range 0.63 - 0.69 were obtained. The rate of the reaction was found to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant, and acid). The linear increase in the rate of oxidation with acidity suggested the involvement of a protonated dimetallic Cr(VI) species in the rate-determining step of the reaction.

The reaction has been found to be slowest in those solvent mixtures that contained the largest proportions of water, and increasing proportions of acetic acid resulted in an increase in the rate of oxidation. Plots of  $\log k_1$  (the pseudo-first-order rate constant) against the inverse of the dielectric constant were linear, with positive slopes. This suggested an interaction between a positive ion and a dipole, and was in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species.

The reactions were studied over a range of temperature, and it was observed that the Arrhenius equation was obeyed. Plots of  $\log k_1$  against the reciprocal of temperature were linear. The activation energies and the different activation parameters were evaluated. The reactions were characterized by negative entropies of activation. This suggested an ordered transition state, relative to the reactants. The isokinetic temperature, obtained from the plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$ , was 581K. Although current views do not attach much physical significance to isokinetic temperature, a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is usually a necessary condition for the validity of the Hammett equation. It was further found that the values for the free energies of activation ( $\Delta G^\ddagger$ ) were nearly constant, suggesting that the same mechanism operated for the oxidation of all the aliphatic aldehydes studied in this investigation.

There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. This indicated that a one-electron oxidation was unlikely.

The observed order of reactivity for the oxidation of aliphatic aldehydes by QDC showed that :

- (a) Acetaldehyde < Propionaldehyde < Butyraldehyde < Valeraldehyde;
- (b) Isovaleraldehyde < Isobutyraldehyde;
- (c) Caproaldehyde < Heptaldehyde < Caprylaldehyde < Pelargonaldehyde < Caprinaldehyde ; and
- (d) Glutaraldehyde < Glyoxal.

The relative rates of oxidation for the aldehydes indicated that the rate of oxidation was dependent on the length of the alkyl chain of the aldehydes. Electron-releasing groups accelerated the oxidation process by increasing the electron availability at the oxygen of the aldehydic carbonyl group. This would facilitate the attack of the electrophile (protonated QDC).

The rate of oxidation of isobutyraldehyde was faster than that for isovaleraldehyde. This observed order of reactivity was due to the fact that the aldehyde function was closer to the isomethyl group in isobutyraldehyde. This proximity effect would have a direct influence on the reactivities of these two aldehydes, thereby facilitating the attack of the electrophile (protonated QDC).

The observed order of reactivity was glyoxal > glutaraldehyde. The presence of methylene groups between the two aldehyde moieties would decrease the electron availability at the oxygen of the aldehydic carbonyl group. This would prevent the attack of the electrophile (protonated QDC) as more methylene groups were inserted between the two aldehydic groups.

Aldehydes exist in three forms : (a) the hydrated aldehydes ; (b) enol-enolate ion; and (c) the free aldehydes. The species involved in the oxidation of aldehydes could be determined by the kinetic data and product analysis.

Aliphatic aldehydes are extensively hydrated in aqueous solutions. The aldehyde hydrate dissociation constants ( $K_d$ ) pertaining to the reaction :

$$\text{RCH(OH)}_2 \xrightleftharpoons{K_d} \text{RCHO} + \text{H}_2\text{O}$$
 were given. From  $k_1$  (the pseudo-first-order rate constant) and  $K_d$ , two sets of rate constants were computed. Values of

$k_{Hy}$  were obtained by assuming that only the hydrated form appears in the rate law:  $v = k_{Hy} [QDC] [RCH(OH)_2]$ .

Similarly,  $k_A$  was calculated using the concentration of free aldehydes according to the rate law:  $v = k_A [QDC] [RCHO]$ . The correlation with  $k_{Hy}$  supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen transfer reaction between the free aldehyde and QDC was very unlikely. This evidence provided additional support for the mechanistic pathway wherein the slow step was the oxidative decomposition of the chromate ester of the aldehyde hydrate. A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The mechanistic pathway involved the rapid formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2). The overall rate of the reaction would depend on the position of equilibrium (step 1), and the rate of the reaction (step 2).

The slow step of the reaction was the transfer of two electrons in a cyclic system. This electrocyclic mechanism for the oxidation of aldehyde hydrates by QDC involved six electrons; being a Hückel-type system ( $4n + 2$ ), this was an allowed process. This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant

Under the experimental conditions employed in the present investigation, aliphatic aldehydes were oxidized by quinolinium dichromate (QDC), in acid media,

giving the corresponding carboxylic acid in each case. The products obtained were characterized by FT-IR and FT-NMR analyses.

Kinetic data has been presented to establish the mechanistic pathway for the oxidation of aliphatic aldehydes by QDC as proceeding via the hydrated form of the aldehydes.

The data collected demonstrated that the QDC oxidation of aliphatic aldehydes led to the formation of the corresponding carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. Under the present experimental conditions, there was no further oxidation of the products. This study has thus emphasized the efficiency of QDC reacting with aliphatic aldehydes, suggesting the possibility that such reactions could prove to be useful as a general route for the synthesis of carboxylic acids.

## Chapter II – Kinetics of Oxidation of $\alpha$ , $\beta$ -Unsaturated Aldehydes

The present work is a detailed kinetic investigation of the oxidation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes (methacrylaldehyde, acrylaldehyde, crotonaldehyde and cinnamaldehyde) by quinolinium dichromate (QDC), in acid medium, using 50% aqueous acetic acid as the solvent, under a nitrogen atmosphere. The course of the reactions was monitored by observing the disappearance of chromium(VI) at 440 nm, spectrophotometrically. The stoichiometric ratios,  $\Delta[\text{QDC}] / \Delta [\text{substrate}]$ , were in the range 0.66 - 0.69. The rate of the reaction was observed to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant, and acid). The rate of oxidation showed a linear increase with acidity, which suggested the participation of a protonated chromium(VI) species in the rate-determining step.

The role of the solvent in these oxidation reactions was investigated. It was observed that the rate of oxidation increased with a decrease in the polarity of the medium, in going from 40% acetic acid to 60% acetic acid. Plots of  $\log k_1$  against the reciprocal of the dielectric constant were linear, with positive slopes, suggesting an ion-dipole type of reaction.

The effect of changes in temperature on the rate of the reaction was studied, and the Arrhenius equation was found to be valid. The activation energies and the other activation parameters were evaluated. The negative entropies of activation ( $\Delta S^\ddagger$ ) indicated that the transition state formed was considerably rigid, resulting in a reduction in the degrees of freedom of the molecule. The similarities in  $\Delta G^\ddagger$  values for all the substrates arose due to changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values, and

emphasized the probability that all these reactions involved similar rate-determining steps.

It was observed that there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. This indicated that a one-electron oxidation was quite unlikely.

The order of reactivity observed was :

methacrylaldehyde > acrylaldehyde > crotonaldehyde > cinnamaldehyde.

The presence of the methyl group (in methacrylaldehyde), adjacent to the site of reaction (carbonyl group), enhanced the reactivity of methacrylaldehyde over that of acrylaldehyde. In crotonaldehyde, the methyl group was far removed from the site of reaction, and hence its reactivity was much less than that of methacrylaldehyde. The presence of the phenyl group in cinnamaldehyde exerted a deactivating influence on the rate of the reaction, and hence the reactivity of cinnamaldehyde was the lowest in the series.

In the present investigation, the oxidation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes by quinolinium dichromate (QDC) in acid medium, was first-order with respect to the concentrations of each - substrate, oxidant, and acid. The first-order dependence of the rate on QDC concentration supported a reaction pathway proceeding through the hydrate-form of the substrate.

On the basis of the kinetic results obtained in the present investigation, a mechanism was proposed for the oxidation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes by

quinolinium dichromate (QDC), in acid medium, using 50% acetic acid as the solvent.

A cyclic structure for the reaction intermediate would explain all the features of the oxidation reaction. The large negative entropies of activation ( $\Delta S^\ddagger$ ) would be consistent with the formation of a cyclic intermediate in a bimolecular reaction. If the chromium was coordinated through the -OH group (of the aldehyde hydrate), then the formation of the chromate ester would be facilitated. This would increase the ease of oxidation, and the conversion to the corresponding carboxylic acid could then be rationalized. The mechanistic pathway involved the formation of the ester of the aldehyde hydrate (step 1), followed by the slow oxidative decomposition of this ester (step 2).

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation that a kinetic isotope effect was observed for the oxidation of the respective aldehyde- $d_1$  compounds ( $k_H/k_D = 6.2$ ), indicating a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction. This step would envisage a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system ( $4n+2$ ), this was an allowed process. This mechanism was supported by the observation that the oxidation reactions were acid-catalyzed. Protonation of the oxidant would make it more amenable towards nucleophilic attack by the substrate on the electron-deficient chromium of the oxidant.

Under the experimental conditions employed in the present investigation,  $\alpha$ ,  $\beta$ -unsaturated aldehydes were oxidized by quinolinium dichromate (QDC), in acid media giving the corresponding carboxylic acids in each case. The products obtained were characterized by FT-IR and FT-NMR analyses.

The data collected demonstrated that the QDC oxidation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes led to the formation of carboxylic acids, substantiating the mechanism wherein there was an attack of the oxidant on the aldehyde hydrate. There was no cleavage of the carbon-carbon bond, thus ruling out the possibility of any enolization. This study emphasized the efficiency of QDC reacting with  $\alpha$ ,  $\beta$ -unsaturated aldehydes, suggesting the possibility of a regioselective route for the synthesis of carboxylic acids.

### Chapter III – Kinetics of Oxidation of Heterocyclic Aldehydes

The kinetics of the quinolinium dichromate (QDC) oxidation of heterocyclic aldehydes (2-furaldehyde, 5-methyl-2-furaldehyde, 5-bromo-2-furaldehyde, 2-pyrrolecarbaldehyde, 2-thiophenecarbaldehyde, 2-pyridinecarbaldehyde and 3-pyridinecarbaldehyde) has been investigated. The reactions were followed by monitoring the absorption band at 440 nm, spectrophotometrically. For all the heterocyclic aldehydes studied, stoichiometric ratios,  $\Delta[\text{QDC}] / \Delta [\text{substrate}]$ , in the range 0.64 – 0.70 were obtained.

Under pseudo-first-order conditions, individual kinetic runs were first order with respect to QDC. Further, the pseudo-first-order rate constants ( $k_1$ ) did not vary with the initial concentration of QDC. The order with respect to the concentrations of aldehydes was unity. The reaction was catalyzed by acid, and the acid-catalyzed reaction showed a first-order dependence on acidity.

The oxidation of heterocyclic aldehydes by QDC was studied in solutions containing varying proportions of acetic acid and water. An increase in the dielectric constant of the medium increased the rate of the reaction. Linear plots of  $\log k_1$  against the inverse of the dielectric constants gave positive slopes, suggesting an ion-dipole type of interaction.

The oxidation of heterocyclic aldehydes was studied at different temperatures (303-323K), and the activation parameters were evaluated. The oxidation of heterocyclic aldehydes was characterized by negative entropies of activation, which

suggested an ordered transition state, relative to the reactants. The similarity in  $\Delta G^\ddagger$  values for all the substrates emphasized the probability that all these reactions involved similar rate-determining steps.

The observed order of reactivity was :

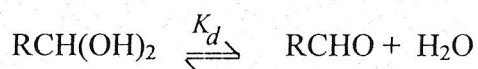
2-furaldehyde > 2-pyrrolecarbaldehyde > 2-thiophenecarbaldehyde, which was in conformity with the decreasing electronegativities of O, N and S atoms (electronegativities were : O = 3.50; N = 3.07; S = 2.44).

For the substituted 2-furaldehydes, the observed order of reactivity was : 5-methyl-2-furaldehyde > 2-furaldehyde > 5-bromo-2-furaldehyde > 5-nitro-2-furaldehyde, which was in conformity with the inductive effects of the substituents.

The observed order of reactivity, in the case of six-membered heterocyclic aldehydes was : 2-pyridinecarbaldehyde > 3-pyridinecarbaldehyde.

It was seen that there was no induced polymerization of acrylonitrile, or the reduction of mercuric chloride, which indicated that a one-electron oxidation was quite unlikely.

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrated form. The experimental rate constants ( $k_1$ ) for the oxidation of the aldehydes by QDC, and the aldehyde hydrate dissociation constants ( $K_d$ ) have been given for the reaction :



From  $k_1$  and  $K_d$ , two sets of rate constants for the oxidation of the aldehyde in only one of the forms present in solution were computed. The values of  $k_{Hy}$  were obtained by assuming that only the hydrate form appears in the rate law:

$$v = k_{Hy} [QDC] [RCH(OH)_2]$$

Similarly, the values of  $k_A$  were calculated using the concentration of free aldehydes according to the rate law:  $v = k_A [QDC] [RCHO]$ .

The correlation with  $k_{Hy}$  supported the mechanistic pathway for the oxidation reactions as proceeding through the hydrated form of the aldehydes. Hence, a mechanism involving a direct hydrogen-transfer reaction between a free aldehyde and QDC was very unlikely. Thus, the rate-accelerating effect of the electronegative substituents could be interpreted in terms of greatly increased hydration. The mechanistic pathway involved the formation of the ester (step 1), followed by the slow oxidative decomposition of the ester of the aldehyde hydrate (step 2).

The slow step of the reaction involved the participation of the aldehyde hydrate, protonated QDC, and two electrons in a cyclic system. Removal of the hydrogen (on the carbon) was part of this step, as evidenced by the experimental observation that a kinetic isotope effect was observed for the oxidation of 2-furaldehyde- $d_1$  ( $k_H/k_D = 5.8$ ). The proton was removed in the cyclic transition state (co-planarity of all the atoms involved), the centre of which resided on an electron-dense oxygen in the chromate ester. Since the five-membered heterocyclic ring system is a planar pentagon with  $sp^2$  hybridized carbon atoms, and possesses a considerable aromatic character arising from delocalization of the two paired

electrons, it would undergo a reaction via an electrocyclic mechanism involving six electrons; being a Hückel-type system ( $4n+2$ ), this was an allowed process.

Under the experimental conditions employed in the present investigation, heterocyclic aldehydes were oxidized by quinolinium dichromate (QDC), in acid media, giving the corresponding carboxylic acids in each case. These products were characterized by FT-IR and FT-NMR analyses.

The data collected demonstrated that the application of QDC to the oxidation of heterocyclic aldehydes led to the formation of carboxylic acids, substantiating the mechanism of the oxidation reaction wherein there was an attack of the oxidant on the aldehydic function, leaving the heteroatom site intact. While highlighting the importance of QDC as an oxidant, this study emphasized the efficiency of the reactions of QDC with heterocyclic aldehydes, which could prove to be a regioselective route for the synthesis of carboxylic acids.

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