Kinetics of the Oxidation of Heterocyclic Aldehydes by Quinolinium Dichromate

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Quinolinium dichromate in sulfuric acid oxidizes heterocyclic aldehydes (2-furaldehyde, 2-pyrrolecarbaldehyde, 2-thiophenecarbaldehyde) to the corresponding acids in a 50% (v/v) acetic acid–water medium. The kinetic data on the rates of oxidation of the substrates have been discussed with reference to the aldehyde hydration equilibria. The kinetic results support a mechanistic pathway proceeding via a rate-determining oxidative decomposition of the chromate ester of the aldehyde hydrate.

The oxidation of heterocyclic aldehydes by Mn(VII) had highlighted the kinetic aspects and nature of the formed product.[1] Cerium(IV) ion in an acetic acid (25%, v/v) medium was used to oxidize 2-furaldehyde to the acid; the reaction involved a free-radical mechanism.[2] Thallium(III) was used for the oxidation of 2-furaldehyde in a perchloric acid solution, and it was observed that the rate of the reaction did not depend on the concentration of H^+ ions.[3] The kinetics of the oxidation of heterocyclic aldehydes by bromic acid in a H_2SO_4–HOAc medium showed that the reaction was first-order both in the oxidant and substrate concentrations, but showed a second-order dependence on the concentration of H^+ ions.[4] Kinetic studies on the oxidation of 2-furaldehyde by chromic acid[5] and quinolinium chlorochromate[6] in acetic acid water media showed a first-order dependence each on the concentrations of the substrate, oxidant and hydrogen ions.

In the oxidation of heterocyclic aldehydes, there exists the possibility of the reaction taking place either at the heteroatom or at the aldehydic function. The aims of the present investigation were: (a) to highlight the effect of the heteroatom on the rate of the reaction and (b) to determine the site of attack of the oxidant. For this purpose, we carried out a kinetic study of the oxidation of heterocyclic aldehydes (2-furaldehyde, 2-pyrrolecarbaldehyde and 2-thiophenecarbaldehyde) by a chromium(VI) reagent, quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in an acid medium, in 50% acetic acid–water (v/v), under a nitrogen atmosphere. This study forms part of our continuing efforts concerning the oxidation of organic substrates by quinolinium dichromate in general,[7] and aldehydes in particular.[8]

Experimental

Materials and Methods. 2-Furaldehyde (S.D. fine chemicals co.) and 2-thiophenecarbaldehyde (Aldrich) were purified by distillation under reduced pressure. 2-Pyrrolecarbaldehyde (Aldrich) was recrystallized before use. The oxidant, quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], was prepared by the reported method,[9] and its purity was checked by spectral analysis. The infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730 cm^{-1}, characteristic of the dichromate ion. Acetic acid (SD, AR grade) was distilled before use. Sulfuric acid (E. Merck) was used after a check of its physical constants. IR spectra were recorded on a FT-IR (DA- 8, Bomen) spectrophotometer.

The method used for the kinetic determinations was described earlier.[7]

Product Analysis. Thirty cm^3 of water was taken and cooled in ice. Concentrated H_2SO_4 (7.9 g, 0.08 mol dm^{-3}) was added slowly with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g, 0.02 mol dm^{-3}) was added and the mixture was warmed to 313 K for complete dissolution of the QDC. To this mixture, 0.015 mol dm^{-3} of a substrate (1.45 g of 2-furaldehyde, 1.43 g of 2-pyrrolecarbaldehyde, and 1.69 g of 2-thiophenecarbaldehyde), taken in 25 cm^3 of 50% acetic acid-water solution, was added. The reaction mixture was stirred at 313 K for 48 h under nitrogen. The organic layer was extracted thrice with ether (25 cm^3 each time), and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4. The oxidized products (2-furancarboxylic acid from 2-furaldehyde; 2-pyrrolecarboxylic acid from 2-pyrrolecarbaldehyde; and 2-thiophenecarboxylic acid from 2-thiophenecarbaldehyde) were obtained after the complete removal of ether (melting points were in agreement with literature values ; yields ≈ 85–90%). Each reaction product was subjected to IR (KBr) analysis, and characterized as follows: (i) 2-Furancarboxylic acid: ν = 3000, 2860 (br, s, –OH), 2583, 1690 (s, C=O), 1470, 1305, 1245, 1020, 930, 760 cm^{-1}, (ii) 2-Pyrrolecarboxylic acid: ν = 3000, 2850 (br, s, –OH), 1692 (s, C=O), 1545, 1355, 1105, 925, 750 cm^{-1}, (iii) 2-Thiophenecarboxylic acid: ν = 3090, 2850 (br, s, –OH), 2621, 1690 (s, C=O), 1530, 1350, 1100, 910, 750 cm^{-1}.

Results and Discussion

The oxidation of heterocyclic aldehydes (2-furaldehyde, 2-pyrrolecarbaldehyde, 2-thiophenecarbaldehyde) by QDC resulted in the formation of the corresponding acids. Under the present experimental conditions, there was no further oxidation of the acids.

The stoichiometry of the reaction was determined.[7] Stoichiometric ratios, Δ[QDC]/Δ[substrate], in the range 0.66 to 0.69 were obtained, which conformed to the following overall equation:

$$3\ C_5H_4O_2 + 2\ Cr^{VI} + 3\ H_2O \rightarrow 3\ C_5H_4O_3 + 2\ Cr^{III} + 6\ H^+ \quad (1)$$
(2-furaldehyde).

Using pseudo-first-order conditions, individual kinetic runs were observed to be first order in QDC. The pseudo-first-order rate constants (k) were independent of the initial concentration of the oxidant (Table 1). The order of the reaction with respect to the substrate concentration was obtained by varying the aldehyde concentration and observing the effect on the rate at constant [QDC] and [H^+]. The results are given in Table 1. The order with respect to the concentration of acid was obtained at constant aldehyde and QDC concentrations. The data given in Table 1 indicate a first-order dependence on the concentration of the acid. Under the acid concentrations used in the present investigation, the protonation of the aldehydes would be less significant. The possibility of the aldehydes getting protonated can be ruled out on the basis that aldehydes are extensively hydrated in an aqueous medium, and are present as equilibrium mixtures of the carbonyl and hydrated forms. The formation constants are thus not dependent on the acidity or alkalinity.[10] Hence, it would be justified to propose that in the range of acid concentrations used, the oxidant QDC was converted to the protonated chromium(VI) species. Earlier reports have established the involvement of protonated Cr(VI) species in chromic acid oxidation reactions.[11,12]

The oxidation of the substrates by QDC was studied over the temperature range 303–323 K; the rate data and activation parameters are given in Table 2. The negative values of ΔS^* provided support for the formation of a rigid activated complex.

The oxidation of the substrates was studied in solutions containing varying proportions of water and acetic acid. The dielectric constants (D) of water–acetic acid mixtures were calculated from the dielectric constants of the pure solvents (at 313 K: water = 73.28, acetic acid = 6.29).[13] It was observed that there was an increase in the rate of the reaction with a decrease in the dielectric constant of the medium (Table 3).

There was no induced polymerization of acrylonitrile or a reduction of mercury(II) chloride,[14] which indicated that a one-electron oxidation was quite unlikely. Control experiments, performed in the absence of a substrate, did not show any appreciable change in the concentration of QDC.

Table 1. Rate Data for the Oxidation of Heterocyclic Aldehydes at 313 K

10^2 [Substrate] / mol dm^{-3}	10^3 [QDC] / mol dm^{-3}	[H_2SO_4] / mol dm^{-3}	$10^4\ k$/s^{-1}		
			2-Furaldehyde	2-Pyrrolecarbaldehyde	2-Thiophenecarbaldehyde
1.0	1.0	0.5	1.25	1.18	1.14
2.5	1.0	0.5	3.12	2.91	2.83
5.0	1.0	0.5	6.21	5.90	5.67
7.5	1.0	0.5	9.32	8.71	8.50
10	1.0	0.5	12.5	11.8	11.2
1.0	0.75	0.5	1.22	1.15	1.14
1.0	0.50	0.5	1.25	1.18	1.13
1.0	0.25	0.5	1.24	1.19	1.15
1.0	0.10	0.5	1.27	1.14	1.12
1.0	1.0	0.75	1.88	1.75	1.64
1.0	1.0	1.0	2.50	2.36	2.20
1.0	1.0	1.25	3.20	2.90	2.70
1.0	1.0	1.50	3.80	3.55	3.40

Table 2. Temperature and Activation Parameters[a)] for the Oxidation of Heterocyclic Aldehydes[b)] by QDC

	$10^4\ k$/s^{-1}		
Temp[c)]/K	2-Furaldehyde	2-Pyrrolecarbaldehyde	2-Thiophenecarbaldehyde
303	0.62	0.59	0.56
308	0.94	0.89	0.84
313	1.25	1.18	1.14
318	1.78	1.74	1.71
323	2.54	2.41	2.35
ΔH^* (kJ mol^{-1})	51	54	56
ΔS^* (J mol^{-1} K^{-1})	−152	−145	−142

a) Error limits: $\Delta H^* \pm 2$ kJ mol^{-1}; $\Delta S^* \pm 5$ J mol^{-1} K^{-1}.

b) [Substrate] = 1.0×10^{-2} mol dm^{-3}; [QDC] = 1.0×10^{-3} mol dm^{-3}; [H_2SO_4] = 0.5 mol dm^{-3}.

c) ±0.1 K.

Table 3. Solvent Effect for Oxidation of Heterocyclic Aldehydes[a)] by QDC at 313 K

$H_2O:AcOH$ (%, v/v)	Dielectric constants D	$10^4\ k/s^{-1}$		
		2-Furaldehyde	2-Pyrrolecarbaldehyde	2-Thiophenecarbaldehyde
50:50	39.79	1.25	1.18	1.14
45:55	36.44	1.82	1.58	1.41
40:60	33.09	2.51	2.09	1.78
35:65	29.74	3.80	2.95	2.51
30:70	26.39	6.30	4.27	3.55

a) [Substrate] = 1.0×10^{-2} mol dm^{-3}; [QDC] = 1.0×10^{-3} mol dm^{-3}; [H_2SO_4] = 0.5 mol dm^{-3}.

Mechanism. The kinetic results showed that the rate of oxidation of heterocyclic aldehydes was dependent on the first powers of the concentrations of each (substrate, oxidant and acid). The acid catalysis of the reaction must be related to the structure of the oxidant (QDC), which was converted to a protonated species at the concentrations of the mineral acid used. Quinolinium dichromate (QDC) is a dimetallic species, an anionic condensed form of chromic acid. Aqueous solutions of chromic acid contain ions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$, besides other protonated species such as $H_2Cr_2O_7$, $HCr_2O_7^-$ and H_2CrO_4.[15] The ionization constant for the $HCrO_4^-$ ion, $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$, was 3.0×10^{-7} mol/L; hence, in dilute aqueous acid, the concentration of CrO_4^{2-} ions was negligible. This has been amply substantiated by Michel et al.,[16] who examined the Raman spectra of chromate, dichromate and chlorochromate species, and found that the protonated form of chromate $HCrO_4^-$ did not exist in aqueous solutions of Cr(VI) compounds. The ionization constant for the $HCr_2O_7^-$ ion given by $HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}$ was 0.85 mol/L; hence, in solutions where pH ≥ 1, the ionization may be considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of dilute mineral acid would be $HCrO_4^-$ and $Cr_2O_7^{2-}$. These ions are in equilibrium with each other according to the following equation: $2\ HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, with the value of $K_d = 35.5$. According to this equilibrium, an increase of the hydrochromate concentration should be significant with dilution. When the Raman lines were examined under dilution, it was established that at pH = 11, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion, whereas at pH = 1.2, it was 100% as the $Cr_2O_7^{2-}$ ion.[16] Hence, at concentrations of acid larger than 0.05 M, the dichromate ion (and its protonated forms) would be the predominant species. In aqueous solutions of $K_2Cr_2O_7$, spectral studies have shown that $Cr_2O_7^{2-}$ was the predominant species.[17] In the present investigation, since the concentrations of acid used were in the range 0.5 to 1.5 M (1M = 1 mol dm^{-3}), the dichromate ion (or its protonated form) would be the predominant species. Moreover, the protonated Cr(VI) species would be a more reactive electrophile capable of increasing its rate of coordination to the substrate.

The effect of a change in the solvent composition (water–acetic acid, %, v/v) on the rate of oxidation for the substrates was studied. It was observed that an increase in the water content of the medium showed a decrease in the rate of oxidation (Table 3). The magnitude of this effect could be analyzed by suggesting that, for the equilibrium $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, a decrease in the dielectric constant of medium (increase in the acetic acid content) would favor the dichromate form over the chromate form. If ion-pairs were to be formed in this medium, it would be expected that they would have a higher ion-pair association constant for the dichromate ion, which would again favor the dichromate ion. The absence of any salt effects on the rate of oxidation indicated that the reaction was not of the ion-ion type. If the reaction was assumed to involve two neutral molecules, then the plot of log k versus $(D-1)/(2D+1)$ would have been linear; this was not found to be so. Although the range of dielectric constants used for these reactions was not large, plots of log k versus $1/D$ were found to be linear, with positive slopes, which indicated that the reactions were of the ion-dipole type.[18]

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrate form.[10,19–24] Table 4 lists the experimental rate constants (k) for the oxidation of the aldehydes by QDC. The aldehyde hydrate dissociation constants (K_d) pertaining to the reaction

$$RCH(OH)_2 \overset{K_d}{\rightleftharpoons} RCHO + H_2O \tag{2}$$

are also given. From k 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,

$$v = k_{Hy}[QDC][RCH(OH)_2]. \tag{3}$$

Similarly, the values of k_A were calculated using the concentration of free aldehydes according to the rate law,

$$v = k_A[QDC][RCHO]. \tag{4}$$

The values of k_{Hy} and k_A are given in Table 4. Using the σ^+ values derived from a consideration of the electrophilic substitution for the hetero systems,[25] a plot of log k_{Hy} against σ^+ was linear ($r = 0.9632$), with a slope of $\rho = +3.0$. On the other hand, the correlation of σ^+ with k_A gave a value of $\rho = +0.675$ ($r = 0.994$). 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 (Table 1). It

Table 4. QDC Oxidation of Heterocyclic Aldehydes at 313 K

Aldehydes	K_d	$10^4\ k/s^{-1}$	$k_{Hy}/M^{-2}\ s^{-1}$	$k_A/M^{-2}\ s^{-1}$
2-Furaldehyde	1.29	1.25	16.56 ± 1.28	12.84 ± 1.28
2-Pyrrolecarbaldehyde	0.92	1.18	10.99 ± 0.41	11.94 ± 0.45
2-Thiophenecarbaldehyde	0.84	1.14	9.53 ± 0.17	11.34 ± 0.20

would be pertinent to compare the ρ value of $+0.675$, obtained in this study, with the ρ values obtained for a series of aromatic aldehydes in 91% acetic acid.[26,27] Since aromatic aldehydes were hydrated only to a small extent, the similarity between these values ($\rho = +1.02$ and $+0.77$)[26,27] and our value ($\rho = +0.675$) was satisfactory in that for both cases, small positive values were obtained. The positive value of ρ could be interpreted as being due a superimposed effect of the ring substituents on the hydration equilibrium, wherein it had been shown that all of the aldehydes oxidized by chromic acid were completely hydrated in aqueous solution.[28] Earlier work on the oxidation of benzaldehyde by chromic acid had shown that a Hammett plot of the data yielded a good straight line with a slope $\rho = +1.06$ (Ref. 29). Later work on the chromic acid oxidation of benzaldehyde had shown that the reaction proceeded by way of the chromic acid ester of hydrated benzaldehyde as an intermediate.[30] This similarity provided additional support for the mechanistic pathway suggested in the present investigation, that the rate-determining step was the oxidative decomposition of the chromate ester of an aldehyde hydrate. The hydrated forms of the substrates would remain as undissociated molecules (since [H^+] would be much greater than the dissociation constants of the substrates), in the range of the acid concentrations used in the present study (0.5–1.50 M). It was therefore suggested that the protonated QDC reacted with the hydrated form of the heterocyclic aldehydes to give the corresponding acids.

Since aldehyde hydrates very closely resembled alcohols, both in structure and in many aspects of oxidation, there would be a similarity in the two oxidation reactions. The oxidation mechanism of alcohols by chromic acid had shown that the rate-determining step involved the decomposition of the protonated acid chromate ester.[31] By analogy, the oxidation of aldehydes would proceed via the formation of a similar intermediate (an ester of the aldehyde hydrate), which would undergo decomposition in the rate-determining step. The hydration of the aldehydes was not rate-determining for the oxidation reaction.[32] The ester of the aldehyde hydrate would be in equilibrium with the free aldehyde and the aldehyde hydrate, and could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate.[33] It may be added that the esterification reaction has more utility, since it helps to understand and predict aldehyde oxidation reactions and their relationship to the closely related oxidation of alcohols.

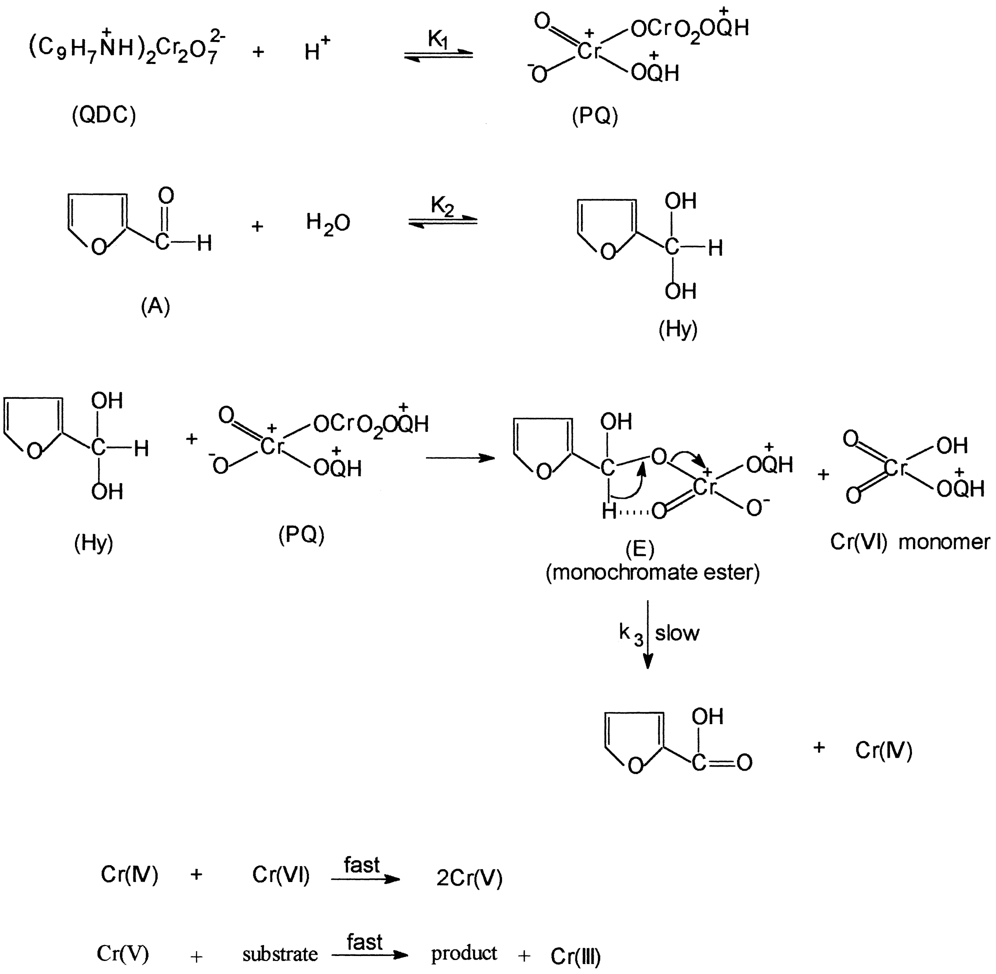
The heteroatoms are strong resonance donors in these five-membered ring systems, an effect which completely overrides their inductive withdrawal. By treating these rings as transmitting systems, one could look for a correlation between the structure and the reactivity of these heterocyclic aldehydes. The observed order of reactivity was 2-furaldehyde > 2-pyrrolecarbaldehyde > 2-thiophenecarbaldehyde (Table 1), 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).[34] The inference was that electronegative substituents increased the oxidation rates by increasing the equilibrium concentrations of the chromate ester of the aldehyde hydrate. This would thus account for the order of the observed reactivity (Table 1).

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). A cyclic structure for the reaction intermediate would explain all of the features of the oxidation reaction. The large negative entropies of activation ($\Delta S^{\neq}$) 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 conversion to the corresponding carboxylic acid could be rationalized.

The manner of electron transfer must be established. Electron flow in a cyclic transition state has been considered,[35] and could be rationalized by assuming that if the chromium was coordinated through the –OH group (of the aldehyde hydrate), then the electron-transfer process could take place through the carbon–oxygen–chromium bond. This would facilitate the formation of the chromate ester, and also enhance the ease of conversion to the product. The proton was removed in the cyclic transition state (co-planarity of all the atoms involved), the center of which resided on an electron-dense oxygen in the chromate ester.[36] Such a transition state envisaged the transfer of electrons towards the chromium, occurring by the formation of the carbon–hydrogen–oxygen bonds, as well as by the carbon–oxygen–chromium bonds.

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 ($k_H/k_D = 5.8$). 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 would be an allowed process.[37] 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 attacks by the substrate on the electron-deficient chromium of the oxidant.

The sequence of reactions for the oxidation of heterocyclic aldehydes by QDC, in an acid medium is shown in the Scheme. In an acid medium, the oxidant QDC was converted to the protonated dimetallic chromium(VI) species (**PQ**) [in the acid range used for the present investigation, the protonated



Scheme 1.

QDC would have the Cr(VI) existing mainly as $Cr_2O_7^{2-}$ (Ref. 17)]. The substrate (**A**) was converted to the hydrated form (**Hy**). The reaction of the hydrated form (**Hy**) with the protonated QDC (**PQ**) resulted in the formation of the monochromate ester (**E**) and a Cr(VI) monomer. The monochromate ester (**E**) underwent decomposition in the rate-determining step to give the product (the corresponding acid), along with the Cr(IV) species. The conversion of Cr(IV) to Cr(III) proceeded by a disproportionation reaction. It was shown that for the reaction Cr(IV) + Cr(VI) → 2 Cr(V), the standard potential for the Cr(VI)–Cr(V) couple was extremely favourable ($E^0 = 0.62$ V),[38] and this reaction would proceed rapidly. The Cr(V)–Cr(III) couple has a potential of 1.75 volt, which would enable the rapid conversion of Cr(V) to Cr(III), after the reaction of Cr(V) with the substrate.[38,39]

If the mechanism shown in the Scheme is correct, then the attack of the protonated QDC (**PQ**) on the aldehyde hydrate (**Hy**) would be crucial, and would be favored by the formation of the cyclic chromate ester (**E**). Based on the mechanism shown in the Scheme, the rate law has been derived as follows:

$$-\mathrm{d}\,[\mathrm{QDC}]/\mathrm{d}t = k_3\,[\mathrm{E}] = k_3\,[\mathrm{Hy}][\mathrm{PQ}], \tag{5}$$

where $[\mathrm{PQ}] = K_1\,[\mathrm{QDC}][\mathrm{H}^+]$, and $[\mathrm{Hy}] = K_2\,[\mathrm{A}]\,[\mathrm{H_2O}]$. Substituting the values of [PQ] and [Hy] in Eq. 5 (taking the activity of water to be unity), we obtain

$$-\mathrm{d}\,[\mathrm{QDC}]/\mathrm{d}t = K_1K_2\,k_3\,[\mathrm{A}][\mathrm{QDC}][\mathrm{H}^+] \tag{6}$$

From this rate expression (Eq. 6), it is clear that the reaction exhibited a first-order dependence with respect to the concentrations of each (substrate, oxidant, and acid). Hence, $-2.303\,\mathrm{d}\log[\mathrm{QDC}]/\mathrm{d}t = k = K_1K_2\,k_3\,[\mathrm{A}][\mathrm{QDC}][\mathrm{H}^+]$. This rate law explains all of the experimentally observed results.

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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