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Oxidation of substituted 2-furaldehydes by quinolinium dichromate: a kinetic study

Girija S. Chaubey, Bansiewdor Kharsyntiew and Mahendra K. Mahanti*

Department of Chemistry, North-Eastern Hill University, Shillong 793022, India

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ABSTRACT: The kinetics of oxidation of substituted 2-furaldehydes by quinolinium dichromate in sulfuric acid, using 50% acetic acid as the solvent, was studied. The rate of the reaction was first order in each of the substrate, oxidant and acid. The kinetic data are 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. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; oxidation; 2-furaldehydes; quinolinium dichromate

INTRODUCTION

The oxidation of heterocyclic aldehydes by Mn(VII) highlighted the kinetic aspects and nature of the product formed.[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 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 H_2SO_4–HOAc medium showed that the reaction was first- order in both 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 on each of the concentrations of substrate, oxidant and acid.

In the oxidation of heterocyclic aldehydes, there is a 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 substituted 2-furaldehydes by a chromium(VI) reagent, quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$], in acidic medium [50% (v/v) acetic acid–water] 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. All the substrates (Aldrich) were purified by distillation under reduced pressure. The oxidant, QDC, 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 (Merck) was used after a check of its physical constants. 2-Furaldehyde-1-*d* was prepared by the reported method.[10] IR spectra were recorded on an FT-IR spectrophotometer (DA-8, Bomem).

Kinetic measurements. The reactions were performed under pseudo-first-order conditions, maintaining a large excess of the substrate with respect to the oxidant. The reactions were performed at constant temperature (0.1 K) and were followed by monitoring the UV-visible absorption band at 440 nm using a DU-650 spectrophotometer (Beckman), as described earlier.[7] All the reactions were performed under nitrogen. The rate constants were evaluated from the linear ($r > 0.996$) plots of log[QDC] against time. The values of the rate constants reported are the means of two or more runs and were reproducible to within ± 3%. The reactions were carried out in aqueous medium, and water–acetic acid mixtures were used for studying the effect of dielectric constant on the rates of the reactions. The reaction mixtures remained homogeneous in the solvent systems used.

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*Correspondence to: M. K. Mahanti, Department of Chemistry, North-Eastern Hill University, Shillong 793022, India.
E-mail: mkmahanti@yahoo.com
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Product analysis. Doubly distilled water (30 ml) was cooled in ice and concentrated H_2SO_4 (7.9 g, 0.08 mol) was added slowly with constant cooling. When the acid solution had cooled to room temperature, QDC (9.52 g, 0.02 mol) was added and the mixture was warmed to 313 K for complete dissolution of the QDC. To this mixture, 0.015 mol of substrate (1.45 g of 2-furaldehyde, 1.66 g of 5-methyl-2-furaldehyde and 1.63 g of 5-bromo-2-furaldehyde), taken in 25 ml of 50% acetic acid–water, was added. The reaction mixture was stirred at 313 K for 48 h under nitrogen. The organic layer was extracted three times with diethyl ether (25 ml each time) and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4. The oxidized products (the corresponding 2-furancarboxylic acids) were obtained after complete removal of the 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: 2-furancarboxylic acid, $\nu = 3000$, 2860 (br, s, OH), 2583, 1690 (s, C=O), 1470, 1305, 1245, 1020, 930, 760 cm^{-1}; 5-Methyl-2-furancarboxylic acid, $\nu = 2860$ (br, s, OH), 1642 (s, C=O), 1525, 1375, 1160, 1030, 940, 760 cm^{-1}; 5-bromo-2-furancarboxylic acid, $\nu = 3130$, 2560 (br, s, OH), 1705 (s, C=O), 1590, 1280, 1160, 940, 760 cm^{-1}; 5-nitro-2-furancarboxylic acid, $\nu = 3120$, 2580 (br, s, OH), 1690 (s, C=O), 1570, 1250, 1170, 930, 760 cm^{-1}.

RESULTS AND DISCUSSION

The oxidation of 2-furaldehydes by QDC resulted in the formation of the corresponding acids. Under the present experimental conditions, there was no further oxidation of the acids.

Stoichiometry

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

$$3C_5H_4O_2 + 2Cr^{VI} + 3H_2O \rightarrow 3C_5H_4O_3 + 2Cr^{III} + 6H^+$$

(2-furaldehyde) (1)

Kinetic results

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. 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 order with respect to the concentration of acid, at constant [aldehyde] and [QDC], was found to be unity. Table 1 shows the kinetic results. In the range of acid concentrations used, the protonation of the aldehydes was less significant,[11] although it cannot be ruled out. It was not possible to decide whether protonation of the aldehydes or protonation of the dichromate resulted in the observed acid catalysis, since these two processes could not be distinguished on the basis of the data obtained. Since the acid concentrations used were in the range 0.5–1.5 mol, the dichromate ion was suggested to be the predominant species in these oxidation reactions. Earlier reports have established the involvement of protonated Cr(VI) species in chromic acid oxidation reactions.[12,13]

Effect of solvent

The oxidation of the substrates was studied in solutions containing varying proportions of water and acetic acid. The dielectric constants (ε_r) 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).[14] It

Table 1. Rate data for the oxidation of substituted 2-furaldehydes at 313 K

			$10^4 k$ (s^{-1})			
[Substrate] (10^2 M)	[QDC] (10^3 M)	[H_2SO_4] (M)	2-Furaldehyde	5-Bromo-2-furaldehyde	5-Methyl-2-furaldehyde	5-Nitro-2-furaldehyde
1.0	1.0	0.5	1.25	1.1	1.5	1.03
2.5	1.0	0.5	3.12	2.6	3.8	2.54
5.0	1.0	0.5	6.21	5.6	7.8	5.12
7.5	1.0	0.5	9.32	8.3	12.1	7.71
10	1.0	0.5	12.5	11.0	15.6	10.2
1.0	0.75	0.5	1.22	1.12	1.52	1.02
1.0	0.50	0.5	1.25	1.09	1.5	1.06
1.0	0.25	0.5	1.24	1.1	1.45	1.01
1.0	0.10	0.5	1.27	1.15	1.43	1.03
1.0	1.0	0.75	1.88	1.7	2.3	1.5
1.0	1.0	1.0	2.50	2.15	3.1	2.05
1.0	1.0	1.25	3.20	2.7	3.7	2.6
1.0	1.0	1.50	3.80	3.4	4.6	3.1

Table 2. Solvent effect for oxidation of substituted 2-furaldehydes[a] by QDC at 313 K

		10^4 k (s^{-1})			
H_2O:AcOH (%, v/v)	Dielectric constant, ε_r	2-Furaldehyde	5-Bromo-2-furaldehyde	5-Methyl-2-furaldehyde	5-Nitro-2-furaldehyde
50:50	39.79	1.25	1.1	1.5	1.03
45:55	36.44	1.82	1.3	2.2	1.24
40:60	33.09	2.51	1.7	3.1	1.5
35:65	29.74	3.80	2.4	4.5	2.2
30:70	26.39	6.30	3.4	7.5	3.2

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

Table 3. Temperature and activation parameters[a] for the oxidation of substituted 2-furaldehydes[b] by QDC

	10^4 k (s^{-1})			
Temperature (±0.1 K)	2-Furaldehyde	5-Bromo-2-furaldehyde	5-Methyl-2-furaldehyde	5-Nitro-2-furaldehyde
303	0.62	0.55	0.75	0.51
308	0.94	0.83	1.1	0.75
313	1.25	1.1	1.5	1.03
318	1.78	1.6	2.1	1.5
323	2.54	2.2	2.8	2.0
$\Delta H^{\neq}$ (kJ mol^{-1})	51	53	49	55
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−152	−151	−157	−148

[a] Error limits: $\Delta H^{\neq}$ ±2 kJ mol^{-1}; $\Delta S^{\neq}$ ±5 J mol^{-1} K^{-1}.

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

was observed that there was an increase in the rate of the reaction with decrease in the dielectric constant of the medium (Table 2). The magnitude of this effect suggested that, for the equilibrium $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, a decrease in the dielectric constant of the medium (increase in the acetic acid content) favored the dichromate form over the chromate form. Although the range of dielectric constants used for these reactions was not large, plots of log k versus $1/\varepsilon_r$ were found to be linear, with positive slopes, which suggested that the reactions were of the ion–dipole type.[15]

Effect of temperature

The oxidation of the substrates was studied over the temperature range 303–323 K; the rate data and activation parameters are given in Table 3. The negative values of $\Delta S^{\neq}$ provided support for the formation of a rigid activated complex which was strongly solvated.

Hydrated form of the substrate

It has been shown that aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrate form.[11,16–21] Table 4 lists the experimental rate constants (k) for the oxidation of the aldehydes by QDC. The aldehyde hydrate dissociation constants (K_d) 10 for the reaction

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

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 calculated. The values of k_{Hy} were obtained by assuming that only the hydrate form appears in the rate law:

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

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

$$v = k_A[QDC]\ [RCHO] \qquad (4)$$

Table 4. QDC oxidation of substituted 2-furaldehydes at 313 K

Aldehyde	K_d	10^4k (s^{-1})	k_{Hy} (M^{-2} s^{-1})	k_A (M^{-2} s^{-1})
2-Furaldehyde	1.29	1.25	16.5 ± 1.28	12.8 ± 1.28
5-Bromo-2-furaldehyde	1.16	1.1	12.7 ± 1.2	10.9 ± 0.27
5-Methyl-2-furaldehyde	1.23	1.5	18.4 ± 1.15	15.5 ± 0.63
5-Nitro-2-furaldehyde	1.09	1.03	11.2 ± 1.0	9.77 ± 0.31

The values of k_{Hy} and k_A are given in Table 4. Using the σ^+ values derived from consideration of the electrophilic substitution for the hetero systems,[22] a plot of $\log k_{Hy}$ against σ^+ was linear ($r = 0.999$), with a slope of $\rho = +0.509$. On the other hand, the correlation of σ^+ with k_A gave $\rho = +0.423$ ($r = 0.979$). This might suggest the involvement of the aldehyde hydrate in the oxidation process. Hence a mechanism involving a direct hydrogen-transfer reaction between a free aldehyde and QDC was very unlikely. Earlier work on the oxidation of benzaldehyde by chromic acid had shown a pathway involving the intermediate formation of the chromic acid ester of hydrated benzaldehyde.[23] This similarity provided additional support for the mechanistic pathway suggested, in the present investigation, that the rate-determining step involved the oxidative decomposition of the chromate ester of the aldehyde hydrate.

Rate law

From the kinetic results, the rate law was derived as follows:

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

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 Eqn (5) (taking the activity of water to be unity), we obtain

$$-d[\mathrm{QDC}]/dt = K_1K_2k_3[\mathrm{A}]\ [\mathrm{QDC}]\ [\mathrm{H}^+] \tag{6}$$

Table 5. Kinetic isotope effect at 313 K[a]

Substrate	$10^4\ k_H$ (s^{-1})	$10^4\ k_D$ (s^{-1})	k_H/k_D
2-Furaldehyde	1.25	—	—
2-Furaldehyde-1-*d*	—	0.215	5.8

[a] [Substrate] = 0.01 M; [QDC] = 0.001 M; [H_2SO_4] = 0.5 M.

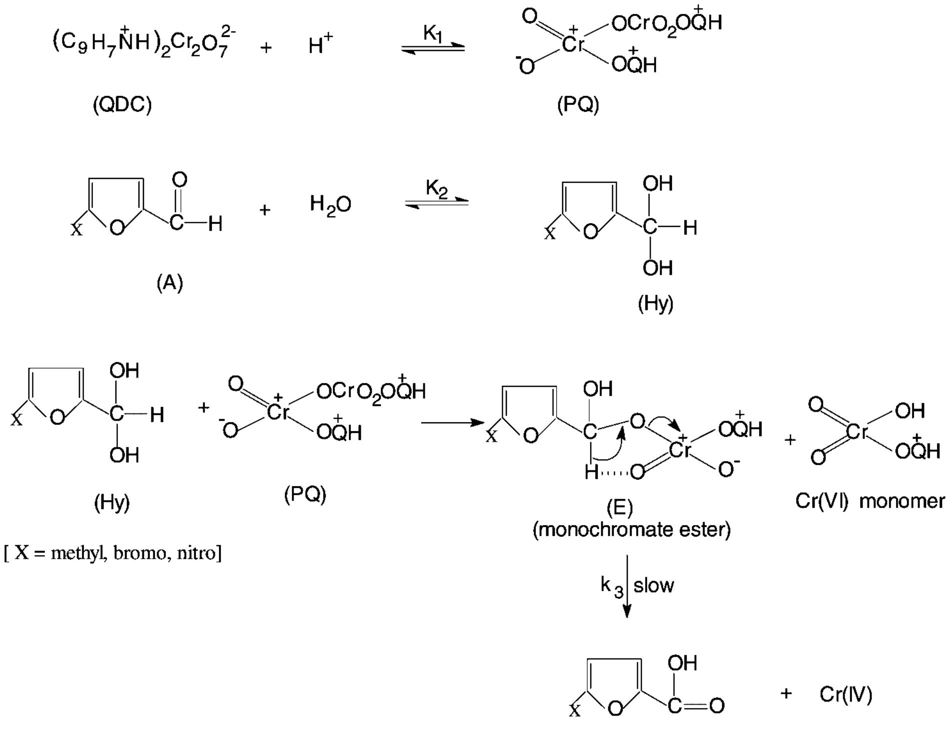
This rate expression shows that the reaction exhibits a first-order dependence with respect to the concentrations of each of the substrate, oxidant and acid. Hence

$$-2.303 d\log[\mathrm{QDC}]/dt = k = K_1K_2k_3[\mathrm{A}]\ [\mathrm{QDC}]\ [\mathrm{H}^+] \tag{7}$$

This rate law explains all of the experimentally observed results.

Structure and reactivity

For the oxidation of the substrates, the order of reactivity is 5-methyl-2-furaldehyde > 2-furaldehyde > 5-bromo-2-furaldehyde > 5-nitro-2-furaldehyde (Table 1), which is in conformity with the inductive effects of the substituents. The inference is that the electron-releasing substituent (methyl) increases the oxidation rate by increasing the equilibrium concentration of the chromate ester of the aldehyde hydrate, and the electron-withdrawing substituent (nitro) decreases the oxidation rate.



Scheme 1

Mechanism

The mechanistic pathway involves the formation of the ester of the aldehyde hydrate (step 1), followed by the slow oxidative decomposition of this ester (step 2). A cyclic structure for the reaction intermediate explains all of the features of the oxidation reaction. The large negative entropies of activation ($\Delta S^{\neq}$) are consistent with the formation of a cyclic intermediate in a bimolecular reaction. Electron flow in a cyclic transition state has been considered,[24] and has been rationalized as follows: if the chromium is coordinated through the OH group (of the aldehyde hydrate), then the electron flow is through the carbon–oxygen–chromium bonds, allowing the formation of the chromate ester and enhancing its ease of conversion to the product.

The slow step of the reaction involves the participation of the aldehyde hydrate, protonated QDC and two electrons in a cyclic system; being a Hückel-type system ($4n+2$), this is an allowed process.[25] Removal of the hydrogen (on the carbon) is part of this step, as evidenced from the kinetic isotope effect for the oxidation of 2-furaldehyde-1-*d* (Table 5), indicating cleavage of the carbon–hydrogen bond in the rate-determining step of the reaction.

The sequence of reactions for the oxidation of heterocyclic aldehydes by QDC has been shown (Scheme 1). In acidic medium, the oxidant QDC is converted to the protonated dimetallic chromium(VI) species (**PQ**). The substrate (**A**) is converted to the hydrated form (**Hy**). The reaction of the hydrated form (**Hy**) with the protonated QDC (**PQ**) results in the formation of the monochromate ester (**E**) and a Cr(VI) monomer. The monochromate ester (**E**) undergoes 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) proceeds by a disproportionation reaction.[26,27]

The data collected demonstrate that the application of QDC to the oxidation of heterocyclic aldehydes leads to the formation of carboxylic acids, substantiating the mechanism of the oxidation reaction wherein there is 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 emphasizes 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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