OXIDATION OF HETEROCYCLIC ALDEHYDES BY QUINOLINIUM DICHROMATE : A KINETIC STUDY

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Abstract. Quinolinium dichromate in sulfuric acid, in 50% (v/v) acetic acid – water medium, oxidized heterocyclic aldehydes to the corresponding acids. The kinetic results supported a mechanistic pathway proceeding via a rate – determining oxidative decomposition of the chromate ester of the aldehyde hydrate.

Introduction

Owing to its reactivity, selectivity and regiospecificity, quinolinium dichromate [QDC, $(C_9H_7N^+H)_2Cr_2O_7^{2-}$] has been extensively used for diverse transformations such as the oxidation of hydrocarbons,[1] oxidative cleavage of unsaturated compounds,[2] oxidation of cyclic and bicyclic alcohols,[3] amino acids,[4] diols,[5] α-hydroxy acids,[6] ketones,[7] and aldehydes.[8] In the oxidation of heterocyclic aldehydes, there exists the possibility of the reaction taking place either at the heteroatom or at the aldehydic function. We have carried out a kinetic study of the oxidation of heterocyclic aldehydes (pyridine-2-aldehyde and pyridine-3-aldehyde) by QDC, in acid medium, in 50% acetic acid – water (v/v), under a nitrogen atmosphere.

Results and Discussion

The oxidation of heterocyclic aldehydes (pyridine-2-aldehyde and pyridine-3-aldehyde) by QDC resulted in the formation of the corresponding acids. The oxidation reactions were carried out as follows: 15 ml of water was taken and cooled in ice. Concentrated H_2SO_4 (7.9g, 0.08 mol dm^{-3}) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 4.76g, 0.01 mol dm^{-3}) was added and the mixture was warmed to 40°C for complete dissolution of the QDC. To this mixture, 0.015 mol dm^{-3} of substrate (1.61g), taken in 25ml of 50% acetic acid-water solution, was added. The reaction mixture was stirred at 50°C for 48h under nitrogen. The organic layer was extracted thrice with ether (25ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4. The oxidized products (pyridine-2-carboxylic acid from pyridine-2-aldehyde; pyridine-3-carboxylic acid from pyridine-3-aldehyde) were obtained after the complete removal of ether (yields ≈ 85-90%).

The method used for the kinetic determinations has been described earlier.[5] 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 (Table 1). The acid catalysis of the reaction was related to the structure of the oxidant (QDC), which was converted to a protonated dimetallic chromium (VI) species (**PQ**). It was observed that having the aldehydic function at the 2-position or the 3-position had a marginal effect on the rate of the reaction, with the 2-isomer reacting faster than the 3-isomer. This suggested that the geometric requirement of the interaction of the aldehydic function with the protonated QDC in the transition state was relatively insensitive to any steric effects.

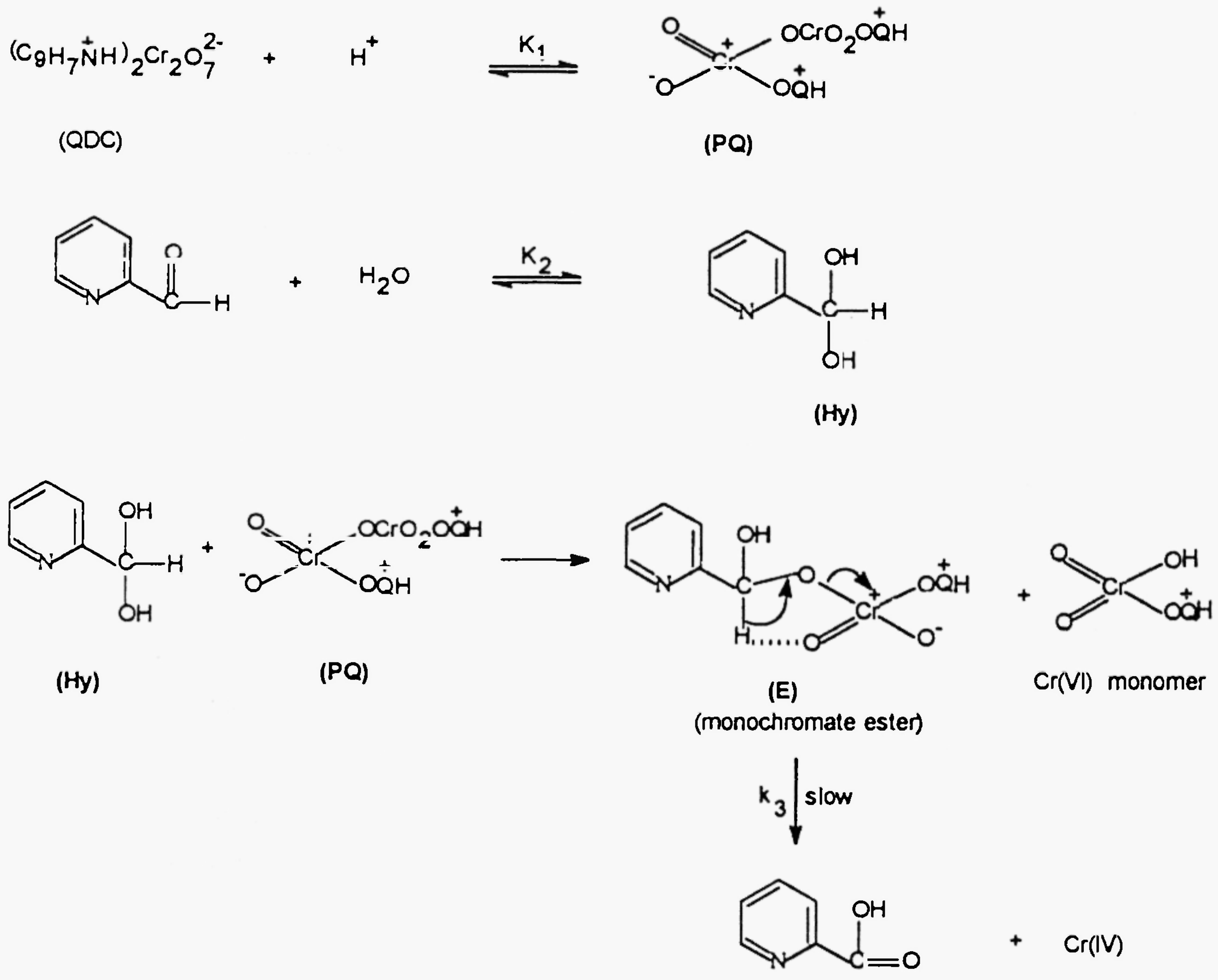
Aldehydes are extensively hydrated in aqueous solutions and many oxidation reactions proceed via the hydrate form.[9-15] The oxidation of heterocyclic aldehydes (in the hydrated form, **Hy**) thus proceeded via the formation of an ester of the aldehyde hydrate (**E**), which underwent decomposition in the rate-determining step. This ester could be formed either by a carbonyl addition reaction to the free aldehyde or by esterification of the hydrate (**Hy**). 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.[16]

The mechanistic pathway (Scheme) 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 (**Hy**), protonated QDC (**PQ**), 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 pyridine-2-aldehyde-d$_1$ ($k_H / k_D = 5.8$). Since the six-membered heterocyclic ring system is a planar hexagon with sp^2 hybridized carbon atoms and possesses considerable aromatic character, the aldehydic function would undergo reaction via an electrocyclic mechanism involving six electrons. Being a Hückel-type system (4n+2), this would be an allowed process.[17]

Table 1 Rate Constants for the Oxidation of Heterocyclic Aldehydes by QDC, in 50% Acetic Acid - Water at 50 °C

[Substrate] x 10^2 mol dm^{-3}	[QDC] x 10^3 mol dm^{-3}	[H_2SO_4] mol dm^{-3}	10^4 k / s^{-1} Pyridine-2-aldehyde	Pyridine-3-aldehyde
1.0	1.0	0.5	2.3	2.0
5.0	1.0	0.5	12.3	10.1
10.0	1.0	0.5	24.0	20.0
1.0	0.5	0.5	2.3	2.0
1.0	0.1	0.5	2.3	2.1
1.0	1.0	1.0	4.6	4.2
1.0	1.0	1.5	7.0	6.0

SCHEME



$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \xrightarrow{\text{fast}} 2\mathrm{Cr(V)} \xrightarrow[\text{fast}]{\text{substrate}} 2\mathrm{Cr(III)}$$

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