Oxidative Properties of Quinolinium Dichromate

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Abstract—In acid medium, quinolinium dichromate oxidized aromatic acids to the corresponding hydroxybenzoic acids, and dicarboxylic acids to the corresponding semialdehydes. The rate of the reaction showed a first order dependence on the concentrations of substrate, oxidant and acid. For the oxidation of the aromatic acids, the rate-determining step involved the formation of a cyclic chromate ester, which underwent decomposition to give the product. In the case of dicarboxylic acids, the mechanistic pathway was via the formation of the intermediate acyclic chromate ester which underwent decomposition, in the slow step, to give the product.

INTRODUCTION

Earlier investigations had reported the decarboxylation of aromatic acids using different oxidizing agents, and the products obtained were mainly phenols [1–10]. The periodate oxidation of salicylic acid had yielded 1,4-benzoquinone-2-carboxylic acid [11]. However, kinetic aspects on the oxidation of aromatic acids have not received much attention.

The kinetics and mechanism of the oxidation of dicarboxylic acids have been studied using oxidants such as vanadium (V) [12], Co(III) [13], S2O8^{2–} [14], and Ce(IV) in acid medium [15–17]. However, the mechanistic pathways described in these investigations did not give any clear evidence for the nature of either carbon-carbon or carbon-hydrogen bond fission.

With a view to highlight the kinetic features of these oxidation reactions and to examine the nature of the products obtained, we have investigated the oxidation of: (i) aromatic acids (salicylic acid and substituted salicylic acids), and (ii) dicarboxylic acids (glutaric and adipic acids) by quinolinium dichromate [QDC, (C9H7NH+ · 2Cr2O7^{2–})], in acid medium, under a nitrogen atmosphere. This study forms part of our sustained efforts to exploit QDC for the oxidation of organic substrates [18].

EXPERIMENTAL

Materials, methods and stoichiometry
Salicylic acid (S.D. fine Chemicals Co.), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, glutaric acid (SRL), and adipic acid (HPC) were recrystallized before use. Quinolinium dichromate (QDC) was prepared by the reported method [19], and its purity checked by spectral analysis. The infrared spectrum (KBr) exhibited bands at 930, 875, 765, and 730 cm\(^{-1}\), characteristic of the dichromate ion. Sulfuric acid (E. Merck) was used after a check of its physical constants. Acetic acid (S.D., AR grade) was distilled under reduced pressure and the fraction distilling at 116°C was used. Dimethylformamide (DMF) was obtained from Spectrochem and was distilled under reduced pressure. Salicylic acid-d\(^6\) was prepared by the reported method [20]. Deuterium oxide was obtained from the Aldrich Chemical Company. The IR spectra were recorded using the FT-IR (DA-8, Bomem) spectrophotometer.

All the kinetic measurements were performed under nitrogen, using pseudo-first-order conditions, with [substrates] ≫ [QDC]. The method of evaluating rate constants (reproducibility ±3%) has been described earlier [18]. The stoichiometries of the reactions were determined [18] to be:

\[
3C_7H_6O_3 + 2\text{Cr(VI)} + 3H_2O \rightarrow 3C_7H_6O_4 + 2\text{Cr(III)} + 6H^+ ,
\]

(Salicylic acid)

\[
C_8H_8O_4 + 2\text{Cr(VI)} + H_2O \rightarrow C_4H_6O_3 + CO_2 + 2\text{Cr(IV)} + 4H^+ .
\]

(Glutaric acid)

1 This article was submitted by the authors in English.
Table 1. Rate data for the oxidation of aromatic and dicarboxylic acids at 323 K

<table>
<thead>
<tr>
<th>[Substrate] × 10^2, M</th>
<th>[QDC] × 10^3, M</th>
<th>[H_2SO_4], M</th>
<th>k_1* × 10^4, s^-1</th>
<th>k_2** × 10^2, s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>salicylic acid (1)</td>
<td>3-hydroxybenzoic acid (2)</td>
<td>4-hydroxybenzoic acid (3)</td>
<td>2,4-dihydroxybenzoic acid (4)</td>
<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>3.0</td>
<td>0.37</td>
<td>0.18</td>
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<tr>
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<td>1.0</td>
<td>3.0</td>
<td>1.86</td>
<td>0.91</td>
</tr>
<tr>
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<td>1.0</td>
<td>3.0</td>
<td>3.57</td>
<td>1.85</td>
</tr>
<tr>
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<td>3.0</td>
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<td>3.65</td>
</tr>
<tr>
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<td>0.93</td>
</tr>
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<td>3.5</td>
<td>2.15</td>
<td>1.06</td>
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<td>1.0</td>
<td>5.0</td>
<td>3.12</td>
<td>1.50</td>
</tr>
</tbody>
</table>

* Solvent: H_2O/ACOH = 50 : 50 (vol).
** Solvent: H_2O.

Product analysis

Water (30 ml) was taken and cooled in ice. Concentrated H_2SO_4 (4.2 ml) was added slowly with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (0.5 M) was added and the mixture warmed to 323 K for complete dissolution of the QDC. To this mixture, 0.5 M of substrate (1.73 g salicylic acid, 1.73 g 3-hydroxybenzoic acid, 1.73 g 4-hydroxybenzoic acid, 1.93 g 2,4-dihydroxybenzoic acid, 1.65 g glutaric acid and 1.83 g adipic acid), taken in 25 ml of 50% water-acetic acid and 25 ml of 50% water-DMF solutions, respectively (for aromatic acids and dicarboxylic acids), was added. The reaction mixture was stirred at 323 K for 24 h under nitrogen for completion of the reaction. The organic layer was extracted with ether (3 × 25 ml), and the organic extracts were washed with water and dried over anhydrous Na_2SO_4. The oxidized products (2,6-dihydroxybenzoic acid from salicylic acid; 2,3-dihydroxybenzoic acid from 3-hydroxybenzoic acid; 2,4-dihydroxybenzoic acid from 4-hydroxybenzoic acid; 2,4,6-trihydroxybenzoic acid from 2,4-dihydroxybenzoic acid; succinic semialdehyde from glutaric acid; and glutaric semialdehyde from adipic acid), were obtained after complete removal of ether (melting points were in agreement with literature values; yields ≈80–85%). Each product was characterized by IR (KBr) analysis:

(i) 2,6-dihydroxybenzoic acid: ν = 3448 (b, s, –OH), 3030 (s, ArH str.), 2630 (O–H str.), 1695 (s, C=O), 1613, 1493, 1389 (O–H bend.), 1215 (C–O, str.), 910 (O–H str.), 820 cm

(ii) 2,3-dihydroxybenzoic acid: ν = 3571 (b, s, –OH), 3030 (s, ArH str.), 2630 (O–H str.), 1670 (s, C=O), 1613, 1471, 1370 (O–H bend.), 1200 (C–O, str.), 900 (O–H str.), 752 cm

(iii) 2,4-dihydroxybenzoic acid: ν = 3450 (b, s, –OH), 3040 (s, ArH str.), 2610 (O–H str.), 1680 (s, C=O), 1610, 1350 (O–H bend.), 1220 (C–O, str.), 890 (O–H str.), 780 cm

(iv) 2,4,6-trihydroxybenzoic acid: ν = 3580 (b, s, –OH), 3040 (s, ArH str.), 2610 (O–H str.), 1680 (s, C=O), 1620, 1370 (O–H bend.), 1210 (C–O, str.), 900 (O–H str.), 790 cm

(v) Succinic semialdehyde: ν = 3265, 2981 (br s, –OH), 1712 (s, C=O), 1669, 1202, 920 cm

(vi) Glutaric semialdehyde: ν = 3279, 2988 (br s, –OH), 1705 (s, C=O), 1660, 1240, 928 cm

RESULTS AND DISCUSSION

Kinetic Results

The pseudo-first-order rate constant (k_1) did not change appreciably with changing QDC concentrations.

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