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Short Communicatin

A Novel Method to Quantify the Nucleophilicity of Dihydroxy Benzoic Acid Regioisomers by Polarography

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Abstract

The reduction propensities of 2,6-dihydroxy benzoic acid (2,6-DBA) and 3,5-dihydroxy benzoic acid (3,5-DBA) in aqueous medium using classical polarography have been studied to portray their reactivity in aromatic substitution reactions in terms of their relative nucleophilicity. The half-wave reduction potentials for 2,6-DBA and 3,5-DBA have been found to be 800 and 900 mV respectively indicating lower nucleophilicity for 2,6-DBA than that of 3,5-DBA. These results have been confirmed from complementary data by kinetic studies for the iodination of these two regioisomers. This two-pronged complementary study assesses the reactivity of the two substrates in a quantitative manner.

Keywords: Classical Polarography, 2,6-DBA , 3,5-DBA, Reduction potential, Iodination.

Introduction

Rates of electrophilic aromatic substitution reactions depend on a host of factors such as solvent type, pH of the reaction medium, electrophilicity of the reagent and nucleophilicity of the substrate[1,2]. The effect of each of these factors has been speculated qualitatively but a quantitative assertion has been found lacking in most cases. Iodinated aromatic compounds are precursors of many important medicinal drugs. The inclusion of the halogen atom significantly modifies the hydrophilic properties of these drugs facilitating their penetration in lipid membranes. Hence iodination reactions of aromatic substrates in aqueous solution need to be delved into more deeply to reveal their reactivity and subsequent mechanisms in these reactions. Herein we have attempted a two-pronged complementary study to assess the reactivity of two substrates 2,6-DBA and 3,5-DBA in aqueous medium using classical polarography as well as hydrodynamic voltammetry, in an attempt to portray their relative nucleophilicity in a quantitative manner[3-5]. The reactions studied.

Materials and Methods

Chemicals: Benzoic acid regioisomers: the required weights are taken to prepare the stock solutions in double distilled water.

Potassium iodide: aqueous solution contains 100 fold of potassium iodide.

Buffer solution: the required weight of both NaH_2PO_4 and Na_2HPO_4 are used to prepare the stock solutions in double distilled water and mixing the two solutions at specific volumes to maintain the required pH.

Electrodes: The working electrode – Drops of mercury falling from a capillary connected with a mercury container (DME). The reference electrode is a saturated calomel electrode (SCE).

Polarographic Measurements: The reduction propensities of the two substrates were determined by studying their polarograms at a DME versus SCE. These are a measure of their nucleophilicity.

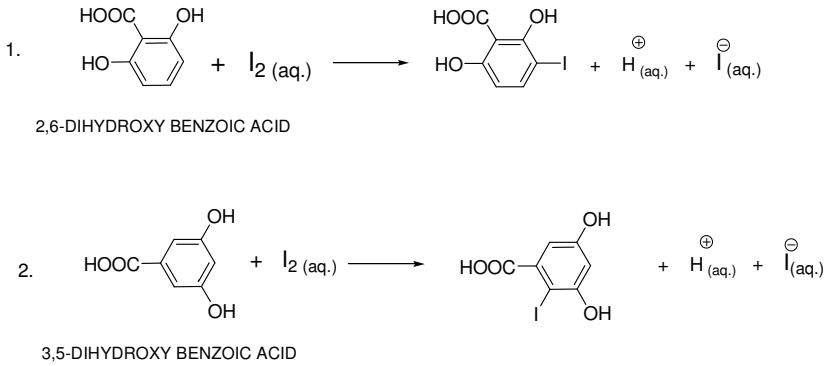

Table-1
Variation of diffusion current with applied voltage for 2,6-DBA, concentration = 1 x 10^{-4} M at 25^0C and pH 6.5, drop rate of mercury = 22/ min

Potential (μV)	Current (nA)	Δid
400	6.8	0.1
500	6.9	0.1
600	7.0	0.1
700	7.1	0.1
800	7.2	0.2
900	7.4	0.1
1000	7.5	0.1
1100	7.6	0.1
1200	7.7	0.1
1300	7.8	-

Table-2
Variation of diffusion current with applied voltage for 3,5-DBA , concentration = 1x 10^{-4} M at 25 ^{0}C and pH 6.5, drop rate of mercury = 22/ min

Potential (mV)	Current (nA)	Δid
400	6.8	0.1
500	6.9	0.1
600	7.0	0.1
700	7.1	0.1
800	7.2	0.1
900	7.3	0.2
1000	7.5	0.1
1100	7.6	0.1
1200	7.7	0.1
1300	7.8	0.1
1400	7.9	-

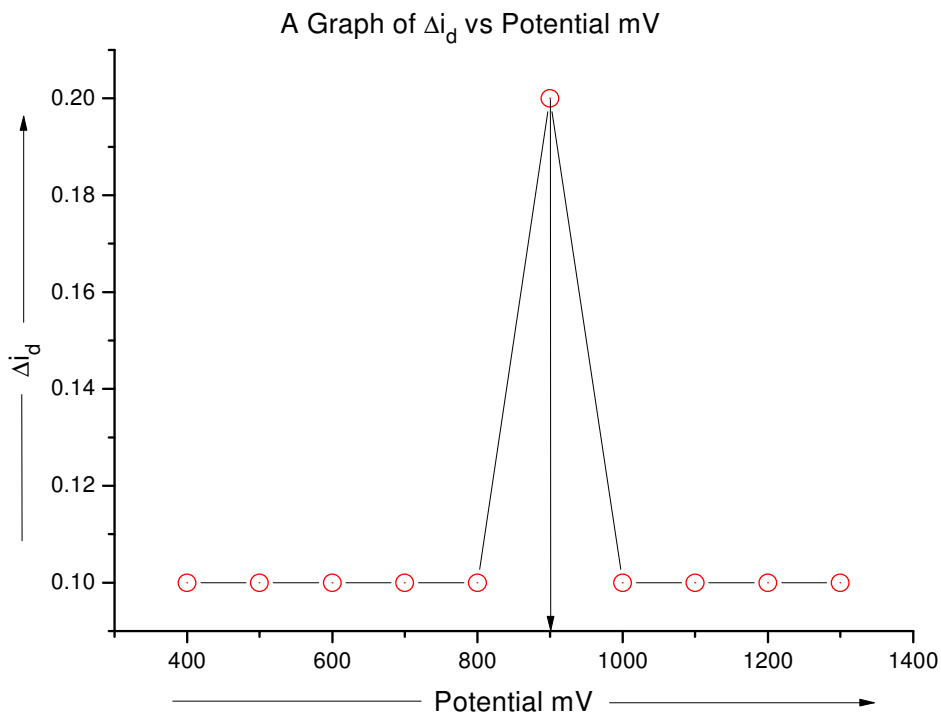

Figure-1
Plot of Δi_d vs potential for 3,5-dihydroxy benzoic acid

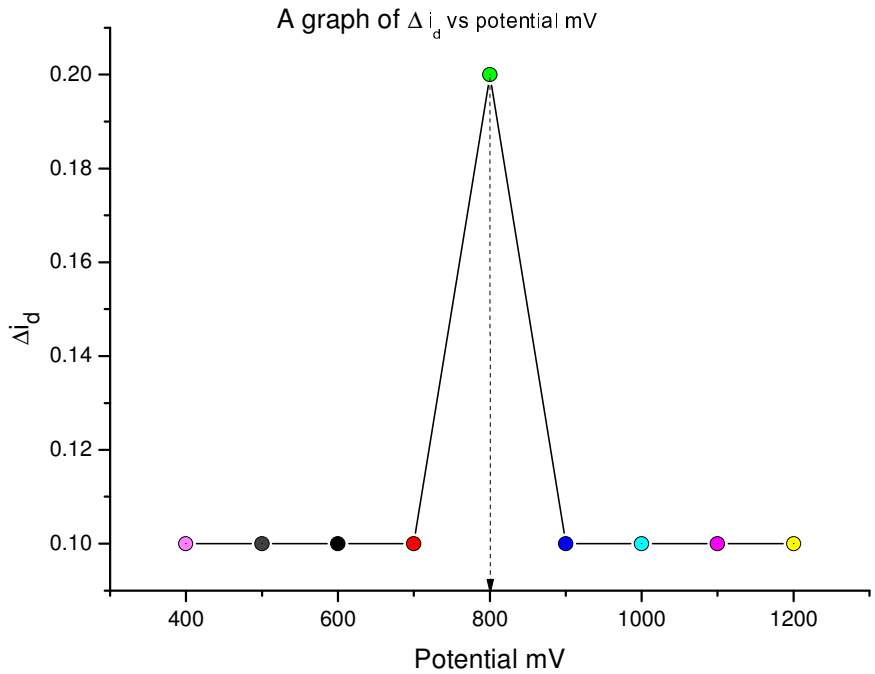

Figure-2
Plot of Δi_d Vs potential for 2,6-dihydroxy benzoic acid

Table-3
Comparison of the parameters studied of 2,6-DBA and 3,5- DBA

Parameter	2,6-DBA	3,5-DBA
Half wave potential ($E_{1/2}$) / mV from polarographic studies	800	900
Specific reaction rate for iodination at 25 ^{0}C / M^{-1} s^{-1} from kinetic studies	1333	2000

Hence, i. Nucleophilicity of 2, 6- DBA < Nucleophilicity of 3, 5- DBA, ii. Reactivity in iodination of 2, 6- DBA < Reactivity in iodination of 3, 5- DBA.

3,5-dihydroxybenzoic acid contains partial negative charges on oxygen atoms at carbon atoms 3 and 5 making 3,5-dihydroxybenzoic acid more nucleophilic towards the electrophile I^+ for substitution at carbon atom 4; than 2,6-dihydroxybenzoic acid.

Conclusion

The substrate having higher $E_{1/2}$ being more nucleophilic should evince a greater iodination rate. This is indeed found to be the case from these studies. The reactivity of the two compounds under study are further assessed from the specific reaction rates for their iodination. These facts have been borne out convincingly from this two-pronged study.

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