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Research Article

RAPID IODINATION OF THE ISOMERS OF AMINOBENZOIC ACID IN AQUEOUS MEDIUM BY IODINE MONOCHLORIDE USING HYDRODYNAMIC VOLTAMMETRY: REGIOSPECIFICITY EFFECT

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Abstract

The rapid kinetics of the iodination of para-aminobenzoic acid and meta-aminobenzoic acid by iodine monochloride at 4.5 pH has been studied by employing hydrodynamic voltammetry. The reactions were found to be of the second order and the specific reaction rates for the two reactions were found to be 25 $M^{-1}s^{-1}$ and 10 $M^{-1}s^{-1}$ at 25.0^{0}C respectively. These data were complemented with those for the iodination of ortho-aminobenzoic acid by ICl obtained earlier to quantitatively assess the relative reactivity of the three isomers stemming from substituent regiospecificity.

Keywords: Iodine monochloride, hydrodynamic voltammetry, aminobenzoic acid isomers.

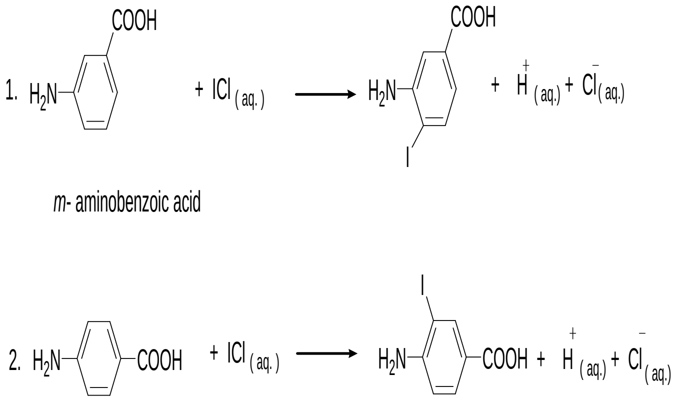
Introduction

Iodine monochloride is an interhalogen compound with the formula ICl (Lee,1996). It is polar and is a potential source of I^+. Iodinations of aromatic substrates in aqueous medium yield iodo derivatives of the substrates that have significance in pharmacodynamics as motiffs of drugs having several antiseptic, disinfectant, antiviral and anti-bacterial properties[2].

The rapidity of halogenations of aromatic substrates in aqueous medium necessitate the use of special techniques to measure the reaction rates (Hernandes, 2010, Borkar, 2013, Dangat et al., 2012). These include temperature jump, stopped flow and pulse radiolysis techniques.

We have herein adopted a relatively simple but efficient technique, hydrodynamic voltammetry, to monitor the rate of the fast iodination of para-aminobenzoic and meta-aminobenzoic by iodine monochloride in aqueous solution.

The reactions studied are as follows :



m- aminobenzoic acid

p- aminobenzoicacid

Iodine monochloride being the only species in the reaction that is electroactive at a microelectrode, its decay as the reaction proceeds is monitored by determining the nanocurrent at a platinum microelectrode that rotates at 600 rpm. The following are the half-cell reactions at the two electrodes in the galvanic cell used in this hydrodynamic voltammetry technique.

$ICl + 2e^- \rightarrow I^- + Cl^-$ **At the positive electrode, RPE**

$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$ **At the negative electrode, SCE**

$ICl + 2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + I^- + Cl^-$ **Overall reaction**

The use of a large concentration of KCl ensures linear proportionality of the diffusion limited snanocurrent at the RPE generated by iodine monochloride.

Preparation of solutions

Iodine monochloride: A stock solution of iodine monochloride is prepared in double distilled water. The strength of this solution is determined iodometrically.

A.R. grade aminobenzoic acid isomers and KCl and are used to prepare the stock solutions in water.

Experimental

Instrumentation

A constant potential of + 0.2 V versus the SCE is applied at the RPE, using a potentiometer.

A galvanometer with the sensitivity of 0.10 nA cm^{-1} provided with a lamp and scale arrangement is employed to register the nanocurrent due to iodine monochloride. The current passing through the galvanometer is controlled by employing a shunt.

Calibration of readings

The two electrodes are dipped in 50.0 cm^3 of 8 × 10^{-2} M KCl, which is the supporting electrolyte at 25.0^{0}C. A potential of + 0.2 V versus the reference electrode is applied at the rotating platinum cathode. The galvanometer light spot is adjusted to zero deflection on the scale. KCl solution is then replaced by 8 ×10^{-4} M iodine monochloride solution containing 8 ×10^{-2} M potassium chloride and the diffusion current reading is set at about 50.0 cm using a shunt. The nanocurrent due to iodine monochloride in the range 2.0 ×10^{-4} M to 8.0 ×10^{-4} M is then recorded without disturbing the shunt for different ICl concentrations[Table 1].The plot of [ICl] versus diffusion current is found to be linear.

The temperature of 25.^{0}0 C is maintained by the use of a thermostat having 0.10 ^{0}C accuracy.

Kinetic measurements

25 cm^3 each of 1.6 × 10^{-3} M para-aminobenzoic acid and iodine monochloride, both containing 0.16 M KNO_3 and the required buffers for 4.5 pH are maintained in a thermostat in separate flasks. The contents of the two flasks are mixed in the reaction vessel containing the electrodes, and stop-clock is simultaneously started.The reducing nanocurrent due to ICl is monitored .

The above procedure of calibration and kinetic measurement is repeated for checking the reproducibility of the galvanometer measurements, and these are found to be within the limits of 0.2 cm.

From the deflections noted during the kinetic study, the unconsumed iodine monochloride, is determined using the calibration plot. A graph of [ICl]$^{-1}$ i.e. 1/(a-x) versus ‘t’ is a straight line ascertaining the order of the reaction to be two.

The gradient of this plot gives the specific reaction rate ‘k’.
The kinetic measurements are repeated for the meta-aminobenzoic acid isomer.

Table 1. Calibration of the diffusion current at 25.0^{0}C

[ICl] / 10^{-4}M	Deflection / nA
1.0	6.3
2.0	12.6
4.0	25.1
6.0	36.2
8.0	50.0

Table 2 Constant parameters in the kinetics of iodination of para-amino benzoic acid in aqueous medium at 25.0^0C AT 4.5 pH

Sr.no.	Parameter	Value	Unit
1	Potential applied at the RPE Vs SCE	0.2	V
2	Initial concentration of iodine monochloride	8×10^{-4}	M
3	Initial concentration of aminobenzoic acid isomer	8×10^{-4}	M
4	Concentration of potassium chloride	8×10^{-2}	M
7	Total volume of the reaction mixture	50	cm^3

Table 3 Kinetics of iodination of para-amino benzoic acid at 25.0^0c by iodine monochloride in aqueous medium at 4.5 pH

Time /s	**Diffusion current / nA**				**$[ICl]/10^{-4}$ M**	**$[ICl]^{-1}/10^3M^{-1}$**
	1	2	3	Mean		
20	34.5	34.6	34.5	34.5	5.71	1.75
30	31.1	31.1	31.0	31.1	5.00	2.00
40	28.1	28.0	28.0	28.0	4.44	2.25
50	25.2	25.0	25.0	25.0	4.00	2.50
60	22.0	22.1	22.0	22.0	3.64	2.75

Results and Discussion

Both the reactions under study are found to follow second order kinetics as the plot of $[ICl]^{-1}$Vs time is a straight line in each of these two cases the slopes of which yield the specific reaction rates for the iodination of the two isomers under study. A typical observation table is shown in Table 3.The predominant iodinating species in this study is ICl since the hydrolysis of ICl to hypoiodous acid is suppressed at pH 4.5 and also due to the large concentration of the KCl used as the supporting electrolyte. The specific reaction rates for the iodination of the three regioisomers are depicted in Table 4.The 3-iodo derivative is the product in both the reactions under study. This is confirmed from NMR characterization.

Table 4: The relative reactivity of the isomers of aminobenzoic acid from kinetic data

Regioisomer	Velocity constant for iodination $/M^{-1}\ s^{-1}$
p-aminobenzoic acid	25
m- aminobenzoic acid	10
o- aminobenzoic acid (Zope, et al.,)	395

Conclusion

The rate of electrophilic aromatic substitution reactions depends on the reactivity of the electrophile and steric considerations. The substrate under study is acidic and a weak nucleophile . The electrophile ICl is moderately strong and the bulkiness of the incoming iodo group offers moderate steric hindrance. The amino group is otho and para directing while the COOH group is meta directing. These factors coupled with steric compulsions of the reaction dynamics, in unison slow down the iodination rate in the meta isomer in comparison with the ortho isomer, the para isomer being moderately reactive. These facts have been quantitatively justified through investigations of the rapid kinetics in the present study.

Green chemistry principles were inherent in the study in view of the short half-lives of the reactions and very low concentrations of the solutions used.

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