The Rapid Iodination of Salicylic Acid in Aqueous Medium by Iodine Monochloride using Hydrodynamic Voltammetry

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Abstract

The rapid kinetics of iodination of salicylic acid by iodine monochloride at 7 pH has been studied at five different temperatures. The reaction is very fast and of the second order, having half-life 300 seconds and rate constant 6.81 $M^{-1}s^{-1}$ at $30.2^{0}C$. The reaction is fast and hydrodynamic voltammetry, a special technique to follow the rapid iodination kinetics is employed. he energy of activation, entropy change in the reaction and the frequency factor in the reaction are evaluated. The kinetic and related thermodynamic data obtained are used to comment on the reactivity of the substrate.

Keywords: Iodine monochloride, hydrodynamic voltammetry, salicylic acid, fast reaction.

Introduction

Iodine monochloride is an interhalogen compound with the formula ICl^{1}. The molecular mass of iodine monochloride is 162.35 g/mol and density is 3.10 gcm^{-3}. It is soluble in CS_2, acetic acid, pyridine, alcohol, ether and water.
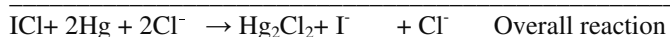
ICl is polar and is a potential source of I^{+}. Iodinations of aromatic substrates in aqueous medium yield iodo derivatives that have significance in pharmacodynamics , as moieties of drugs having antiseptic, disinfectant, antiviral and anti-bacterial properties[2].

The rapidity of halogenations of aromatic substrates in aqueous medium necessitates the use of special techniques to measure the reaction rates[3-5]. These include temperature jump, stopped flow and pulse radiolysis techniques.

We have herein adopted a relatively simple yet efficient technique, Hydrodynamic Voltammetry, to monitor the rate of the fast iodination of salicylic acid by iodine monochloride in aqueous solution.

Iodine monochloride being the lone 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 1000 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 hundredfold molar KNO_3 ensures linear proportionality of the nanocurrent 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.

Salicylic Acid: The required weight of A.R. grade of salicylic acid is used to prepare the stock solutions in water.

Buffer Solutions: Na_2HPO_4 and NaH_2PO_4 each of 0.4 molarity are prepared as buffer solutions.

Potassium Nitrate: A.R. grade potassium nitrate is used to prepare a stock solution of which is used as the supporting electrolyte.

Salicylic acid   5-Iodo Salicylic acid
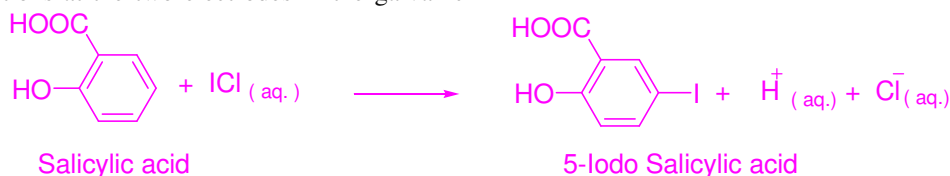
Scheme-1
The reaction between Salicylic acid and ICl

Material and Methods

Construction of the RPE: The rotating platinum electrode (RPE) consists of a 0.5 mm diameter platinum wire fused to one end of inverted 'T' shaped glass tube having 6 mm diameter, such that a centimeter of the platinum wire protrudes out[6,7]. A pulley and a pair of ball-bearing are mounted on this glass tube, having the total length of 32 cm. The ball bearings are fixed to a stand. A pulley is connected to a synchronous motor. The radius of the pulley is so adjusted that the electrode rotates at a speed of 600 rpm. Some mercury kept inside the glass tube and a silver wire is inserted for electrical contact. The lower 4cm portion of the glass tube effects a stirring action in the solution when the electrode is rotated. A constant potential of + 0.1V versus the saturated calomel electrode (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 5×10^{-2}M KNO$_3$ which is the supporting electrolyte. + 0.1V versus the reference electrode is applied at the rotating platinum cathode. The galvanometer light spot is adjusted to zero deflection on the scale. KNO$_3$ solution is then replaced by 5×10^{-4} M iodine monochloride solution containing 5×10^{-2} M

potassium nitrate. The nanocurrent due to iodine monochloride in the range 1×10^{-3} M to 5×10^{-4} M is recorded. A typical calibration plot is depicted in figure1.

The procedure is repeated at five different temperatures using a thermostat.

Kinetic Measurements: 25 cm^3 of 1×10^{-3}M salicylic acid containing 0.1M KNO$_3$ and 1×10^{-3} M iodine monochloride containing 25 cm^3 of 0.1 M potassium nitrate containing Na$_2$HPO$_4$ and NaH$_2$PO$_4$ are maintained in a thermostat in separate flasks. While mixing the contents of the two flasks in the reaction vessel containing the electrodes, a stop-clock is started and the attenuating 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.

Results and Discussion

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

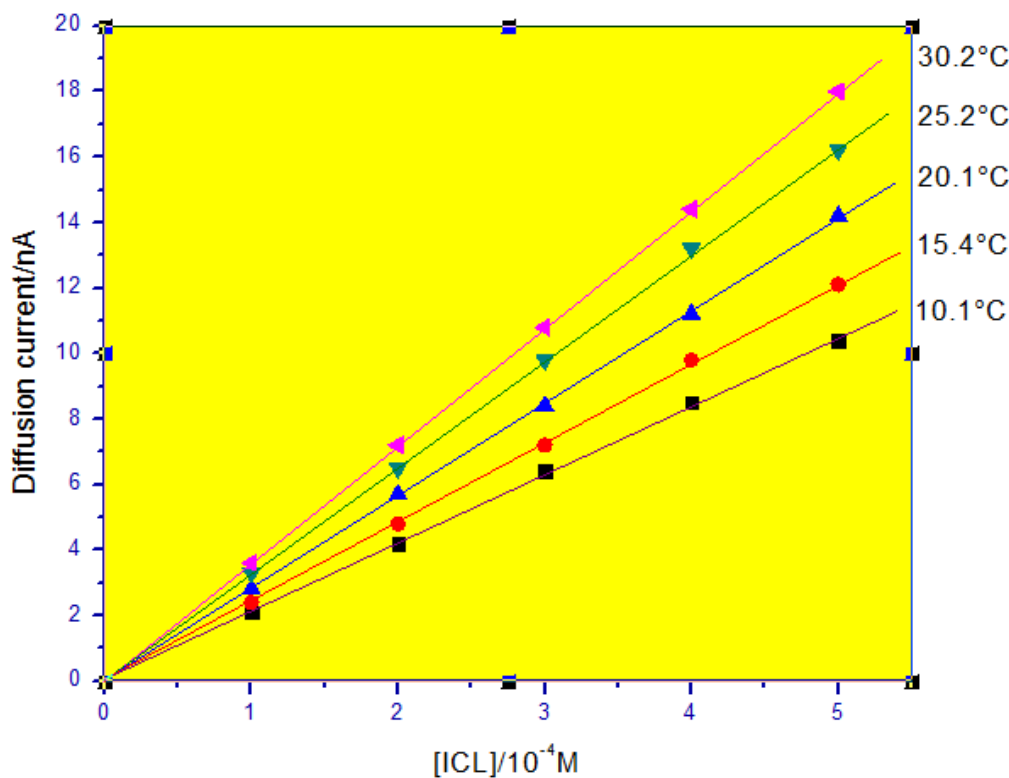The gradient of this plot gives the specific reaction rate 'k'.
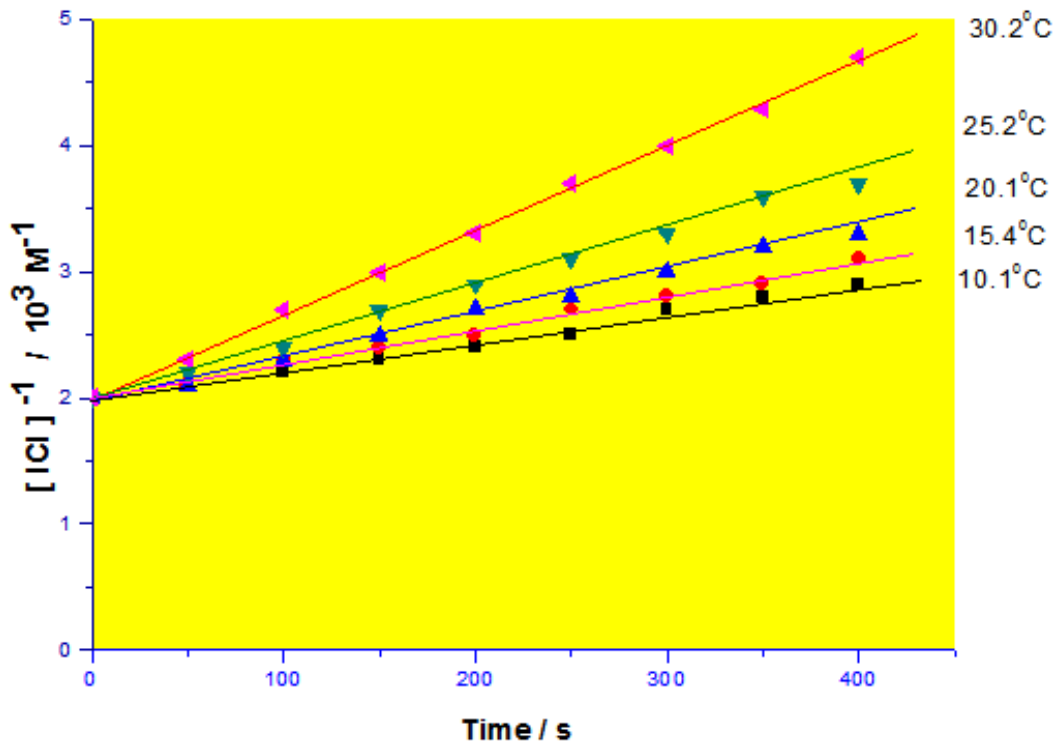

Figure-1
Calibration Plots at various temperatures

Figure-2
Plot of reciprocal of concentration of unconsumed ICl versus time
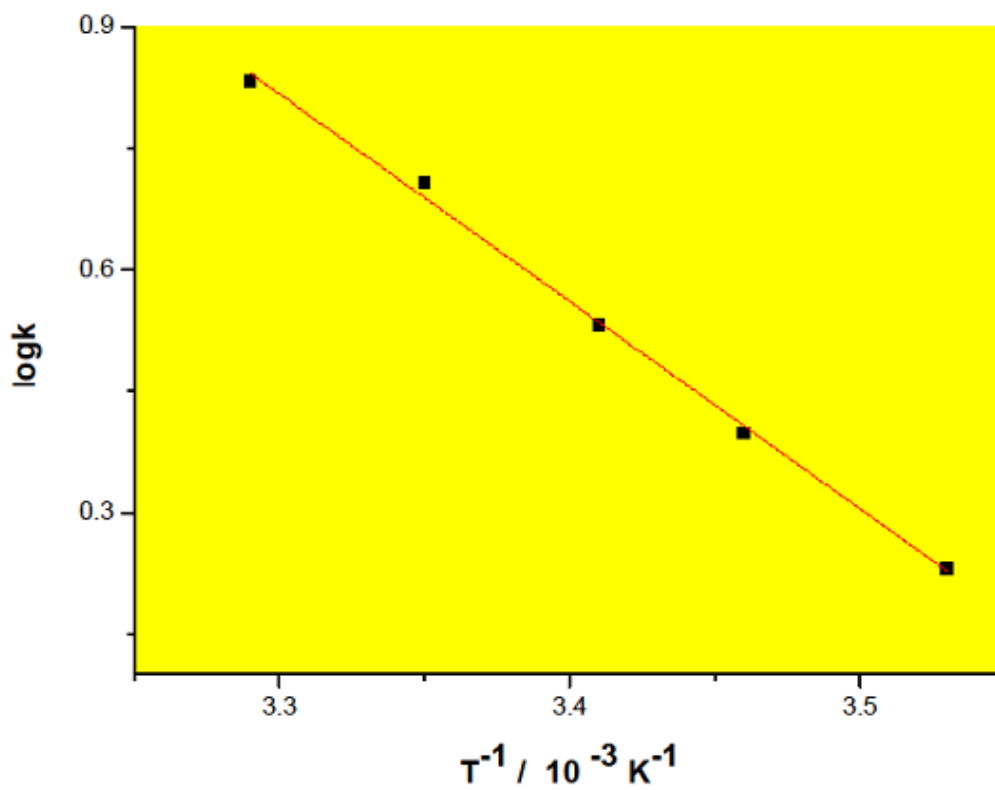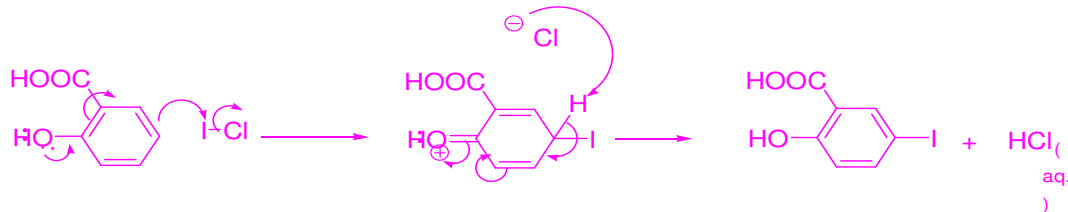

Figure-3
Arrhenius Plot for the iodination of salicylic acid by ICl

Scheme-2
Mechanism of iodination of Salicylic acid by ICl

These studies are repeated in the temperature range 10-30^{0}C, from which the energy of activation, 'E$_a$' for the reaction is evaluated. Further, the frequency factor, A and the entropy change ΔS are also calculated.

Table-1
Calibration of the diffusion current of iodine monochloride at various temperatures for iodination of salicylic acid (± 0.2 nA error)

[ICl]/10^{-4}M	Diffusion Current/nA				
	10.1°C	15.4°C	20.1°C	25.2°C	30.2°C
1	2.1	2.4	2.8	3.3	3.6
2	4.2	4.8	5.7	6.5	7.2
3	6.4	7.2	8.4	9.8	10.8
4	8.5	9.8	11.2	13.2	14.4
5	10.4	12.1	14.2	16.2	18.0

Table-2
Kinetics of iodination of salicylic acid by using iodine monochloride at 10.1^{0}C (±0.2na error)

Time/s	Diffusion Current/nA	[ICl]/10^{-4} M	[ICl]$^{-1}$/10^3 M^{-1}
0	10.4	5.0	2.0
50	10.0	4.8	2.1
100	9.3	4.5	2.2
150	8.9	4.3	2.3
200	8.7	4.2	2.4
250	8.3	4.0	2.5
300	7.7	3.7	2.7
350	7.5	3.6	2.8
400	7.0	3.4	2.9

Table-3
Variation of rate constant of iodination of salicylic acid by iodine (±0.2 error)

Temp/K	[T]$^{-1}$/10^{-3} K^{-1}	k/M^{-1}s^{-1}	log k
283.1	3.53	1.70	0.2304
288.4	3.46	2.50	0.3979
293.1	3.41	3.41	0.5321
298.2	3.35	5.10	0.7075
303.2	3.29	6.81	0.8331

Conclusion

The rate of electrophilic aromatic substitution reactions depends on the reactivitity of the electrophile, and steric considerations.

The substrate under study is acidic and a weak nucleophile[8]. The electrophile is moderately strong and the bulkiness of the incoming iodo group offers moderate steric hindrance. These factors in unison slow down the iodination rate in comparison with bromination of salicylic acid by bromine in aqueous medium[9]. These facts have been quantitatively justified in the present study.

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