Short Communication

Rapid Kinetics of Chlorination of Thiophene in Aqueous Medium Using Rotating Platinum Electrode

Dangat V.T.*, Bonde S.L., Borkar V.T. and Maske P.D.
Department of Chemistry, Nowrosjee Wadia College, Pune, INDIA

Abstract

The rapid kinetics of the chlorination of thiophene in aqueous solution by molecular chlorine at 7 pH has been studied using the rotating platinum electrode RPE. The specific reaction rate, energy of activation Ea and the pre-exponential factor A, are evaluated. The reaction was found to be rapid and of the second order with a half- life of 24 s at 24.5^0C. The rapidity of the reaction necessitated a special technique RPE,to measure the unreacted chlorine which is the only electroreducible species in the reaction. The studies are aimed at complementing quantitative data for chlorinations of aromatic substrates in aqueous medium in view of possible carcinogens formed during disinfection of drinking waters.

Keywords: Chlorination, rotating platinum electrode (RPE), kinetics, disinfectant.

Introduction

Chlorination of drinking waters leads to the formation of trihalomethanes arising from the reactions of organic substrates with chlorine. Some trace amount of chloroform is formed during the chlorination of phenols and di and trihydroxybenzenes[1]. Chlorinated 3,5-cyclohexadienone and similar intermediates are formed as precursors which have been studied by the membrane introduction mass spectrometry (MIMS) technique[2]. Formation of such toxic products during chlorination of drinking water to disinfect it has invoked much interest in recent years in the field of green chemistry. The need for detail insight into the mechanisms of chlorination reactions of aromatic substrates in aqueous medium through kinetics and other studies thus seems justified.

Marino has studied the halogenations of thiophene in acetic acid[3]. Although numerous investigators have reported kinetic data on the gamut of halogenations of aromatic substrates in non-aqueous medium, the rarity of similar data in purely aqueous medium is glaring. The reason for this lacuna is manifest from the difficulties encountered in following the kinetics of such reactions in aqueous medium which stem from their rapidity. In purely aqueous medium, the halogenations of aromatic substrates, especially brominations and chlorinations are very rapid necessitating special techniques to follow their kinetics instead of conventional titrimetry methods. The half-lives of these reactions are often a few seconds or less and setting up innovative techniques to follow the course of such reactions is a challenging task.

Among halogenations of aromatic substrates, brominations are the fastest and iodinations slowest, albeit catalysts and pH of the reaction medium significantly affect the reaction rates[4,5].

Numerous chlorinating reagents such as acidified solutions of hypohalous acid (HOCl), chloramines (NH_2Cl), chloramine T (chloro-4-methylbenzene sulphonamide, sodium salt), NCS (N-Chlorosuccinamide) and molecular chlorine (Cl_2) are used to carry out these reactions in different medium. In the present study, molecular chlorine (Cl_2) at 7pH in purely aqueous medium has been used to study the chlorination of thiophene.

The reaction presently studied is found to be rapid and a special technique is employed for kinetic investigation. The rotating platinum micro electrode (RPE) has been used to monitor the fall in the concentration of chlorine as the reaction proceeds[6] The reaction is found to be of the second order.

The RPE versus the SCE (saturated calomel electrode) detects very low concentrations of unreacted chlorine which is the only electroreducible species among the reactants and products. The diffusion current measured under these conditions is proportional to the chlorine concentration. The phosphate buffer system, Na_2HPO_4 and NaH_2PO_4 was used to maintain 7.0 pH and a hundred fold concentration of potassium nitrate that of the chlorine concentration was used as the supporting electrolyte. The reaction under study is,
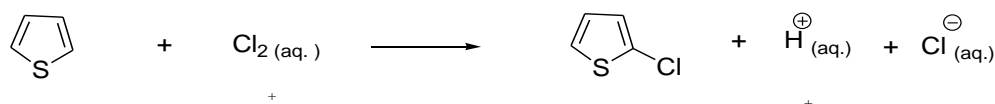
The main product of the reaction is 2-chlorothiophene while the other isomers are formed in traces[7]. The formation of the monochloro isomer has been ascertained stoichiometrically. Among the reactants and products in the reaction, only chlorine is electroreducible at the RPE versus the saturated calomel electrode (SCE) - the reference electrode. Hence the fall in the chlorine concentration as the reaction proceeds is followed in terms of diffusion current as in some reactions reported earlier. The reaction is found to be of the second order and its half-life can be extended by diluting the solutions whereby kinetic measurements can be made at various convenient intervals of time from the start of the reaction.

Material and Methods

Chemicals: AR grade samples of thiophene, sodium dihydrogen phosphate, disodium hydrogen phosphate, potassium nitrate were used to prepare the required stock solutions in double distilled water. Chlorine was prepared from bleaching powder and concentrated hydrochloric acid. It was bubbled through water to free it from HCl and its exact strength was determined from iodometric titration.

Electrodes: The cathode was a platinum electrode fused to a glass tube rotated at 600 rpm with aid of a motor. The anode was a saturated calomel electrode.

Diffusion Current Measurement: Calibration: The RPC and SCE were dipped in chlorine solutions containing the phosphate buffer components for maintaining 7 pH and potassium nitrate which served as the supporting electrolyte. Use of phosphate buffer to maintain constant pH at 7 is common[8]. The concentrations of chlorine in terms of the diffusion current were recorded. The plot of diffusion current Vs [Cl$_2$] were linear.

Table-1
Calibration of diffusion current

[Cl$_2$] / 10^{-4} M	Mean galvanometer deflection/ cm
1.0	10.3
2.0	21.4
3.0	30.2
4.0	40.6
5.0	50.5

pH of the solution = 7.0, Potential applied at the RPE versus SCE = 0.2 volts.
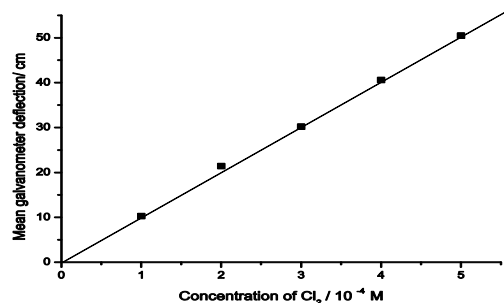
Figure-1
Calibration of diffusion current

Kinetic Measurements: Equimolar solutions of chlorine and thiophene containing the supporting electrolyte and buffer components were kept in a thermostat in different containers. After attaining the desired temperature, these were mixed in the reaction vessel in which RPC and SCE were dipped and a stop clock was simultaneously started. The bent shape of the glass tube to which the RPC is fused ensures efficient mixing of the reactants as the reaction proceeds. At every 10 s the diffusion current in terms of galvanometer light spot is recorded until about the completion of the first half- life of the reaction. A plot of [Cl$_2$]$^{-1}$ Vs time was found to be linear the slope of which is the specific reaction rate. The kinetic measurements were repeated at five different temperatures.

Table-2
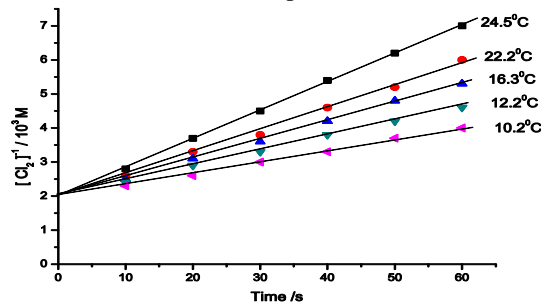**Kinetics of bromination of thiophene by Br$_2$ at 24.5^{0}C in aqueous solution**

Time /s	Diffusion current / cm	[Cl$_2$]/ 10^{-4} M	[Cl$_2$]$^{-1}$/10^3M^{-1}
10	35.7	3.57	2.80
20	27.5	2.70	3.70
30	22.2	2.22	4.50
40	18.5	1.85	5.40
50	16.1	1.61	6.20
60	14.3	1.43	7.00

Initial conc. of chlorine: 5 x 10^{-4} M, Initial conc. of thiophene : 5 x 10^{-4} M, Conc. of potassium nitrate : 5 x 10^{-2} M, Temperature : 24.50^{0}C, pH : 7.0

Table-3
The variation of specific reaction rates of chlorination of thiophene in aqueous medium at different temperatures

Temperature/ K	T^{-1} / 10^{-3} K^{-1}	k/ M^{-1}s^{-1}	log k
283.20	3.530	33.33	1.5228
285.20	3.508	43.48	1.6383
289.30	3.459	55.56	1.7448
293.20	3.410	64.52	1.8097
297.50	3.361	83.33	1.9208

*The specific reaction rate, k, is obtained from the slope of the plot of (Cl$_2$)$^{-1}$ Vs Time at each temperature.

Figure-2
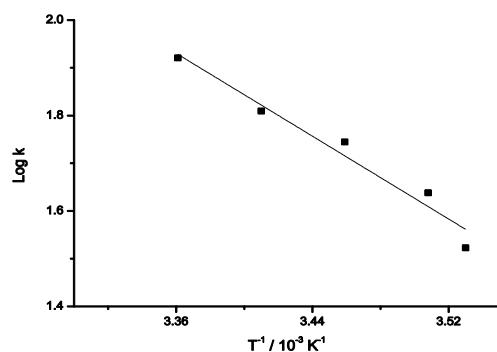**Kinetics of chlorination of thiophene at various temperatures**

Figure-3
Kinetics of chlorination of thiophene: Arrhenius plot

Determination of energy of activation for the reaction: These studies are carried out at various temperatures in the range 10-25^0C, from which the thermodynamic parameters viz. the energy of activation Ea, the pre-exponential factor A, for the reaction evaluated.

Table-4
Kinetic and thermodynamic parameters for the chlorination of thiophene in aqueous medium at 24.5^0C

No.	Parameter	Value
1	Specific reaction rate / $M^{-1}s^{-1}$	83.33
2	Half-life /s	24.00
3	Energy of activation / kJ mol^{-1}	41.60
4	Frequency factor / $10^9 M^{-1} s^{-1}$	1.65

Calculations: Slope of the graph log k Vs T^{-1} = - 2170 $M^{-1}s^{-1}$

Energy of activation: Ea: Ea = -2.303 x R x slope, = 41.60 kJ mol^{-1}

Pre-exponential or Frequency factor: A, k = A exp (-Ea / RT), A = 1.65 X 10^9 $M^{-1}s^{-1}$

Results and Discussion

The plot of $(Cl_2)^{-1}$ Vs time is a straight line the slope of which is the specific reaction rate, unlike a first order reaction.[9] Hence the reaction studied is concluded to follow second order kinetics. The results for the chlorination of thiophene in aqueous solution are shown in tables 1 to 4 and figures-1 to 3. The energy of activation for the reaction was obtained from Arrhenius plot.

Chlorine is the sole chlorinating agent in this reaction since the equilibrium is predominantly shifted to the left in view of the low hydrolysis constant (2.0×10^{-13}) and since hypohalous acid is known to be a very weak electrophile[10].

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$
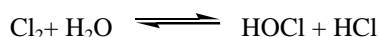
In view of the generally accepted mechanism for electrophilic substitution reactions, the chlorination of thiophene in aqueous solution by molecular chlorine may be explained as follows.

The pi electron cloud of the double bond adjacent to the sulphur atom in the thiophene molecule attacks the one end of the Cl_2 molecule. Subsequently the thiophene molecule loses its aromaticity and becomes unstable. The –ve end of the Cl_2 molecule abstracts the proton in the fast step to stabilize the thiophene molecule in order to re-attribute aromaticity to it. 2-chloro thiophene is obtained with the release of an HCl molecule. The five membered ring of thiophene is less aromatic than the six membered rings of benzene derivatives like aniline and hence only a mono chloro product is formed.
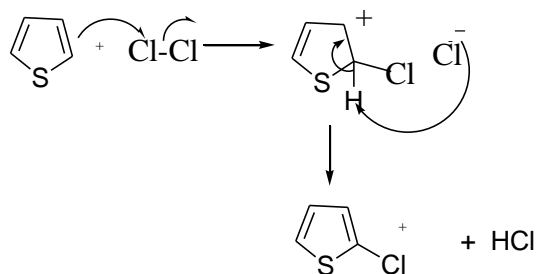
Conclusion

The chlorination of thiophene in purely aqueous solution at 7 pH is a rapid reaction at room temperature leading to the formation of 2-chlorothiophene as the only isomer formed. The RPE technique is necessitated to study the kinetics of the reaction in view of its rapidity. The data obtained in this study is expected to complement those related to the investigation of chlorination reactions of five and six membered aromatic substances. These are useful in the study of possible carcinogenic by-product formation in the chlorination of drinking waters.

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