Structure-Reactivity Correlation of Thiophene and Thiophene-2-Sulfonic Acid by Investigation of Rapid Kinetics of Bromination in Aqueous Medium

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Abstract

The structure-reactivity correlation of thiophene and thiophene-2-sulfonic acid by investigation of the rapid kinetics of bromination in aqueous medium has been carried out employing hydrodynamic voltammetry. The velocity constant for the bromination of thiophene-2-sulfonic acid determined was 106 $M^{-1}s^{-1}$ at 24.5^0C. This value on comparison with that reported under identical conditions for the bromination of thiophene, 526.5 $M^{-1} s^{-1}$ provided a quantitative assessment for the structure related restraints on the reactivity of the two heterocycles under consideration.

Keywords: Bromination, heterocycles, hydrodynamic voltammetry, structure-reactivity correlation.

Introduction

Halogenated aromatic substrates are an important class of compounds in organic synthesis. They are intermediates used to prepare organometallic reagents and are significant in coupling reactions involving transition metals. The halogen functionality accounts for the use of these compounds as medicinal molecules, herbicides, pesticides, fire retardants, disinfectants [1] and other commercially valuable products[2].

Halogenations of aromatic substrates are known to be electrophilic aromatic substitution reactions [3]. Among these, generally brominations are the fastest while iodinations are the slowest[4]. The ease of the electrophilic attack in these reactions is determined by the nature and position of the substituent on the substrate, degree of aromaticity of the substrate, solvent, pH, catalyst and nature of the reagent used, all of which influence the reactivity of the compound undergoing halogenations. The quantitative data is confirming the reactivities of the substrates in these reactions, considering all these factors in a unified manner. The reaction is in aqueous medium so follows the green chemistry principles[5].

Presently, the substituent effect on the reactivity of a five member aromatic heterocyclic compound, thiophene-2-sulfonic acid has been studied by obtaining the rate of its bromination in aqueous medium. This rate is compared with that for the bromination of thiophene in aqueous solution reported under similar conditions. Molecular bromine has been used as the brominating reagent[6]. Kinetics has been used as an investigational tool in these studies to acquire thermodynamic data that enables a quantitative comparison of the reactivity of the two substrates considered herein. The two reactions under study are as follows.

Reaction 2 under study was found to be rapid, like reaction 1 which has been reported under similar conditions[7]. The use of a special technique, hydrodynamic voltammetry, was used to study the kinetics wherein a rotating platinum electrode (RPE) was used for the measurement of the diffusion current (I_D) as a measure of the unreacted [Br_2] which is the only electro-reducible species in the reaction. A saturated calomel electrode (SCE) was used as the reference electrode[8]. In voltammetric and polarographic measurements[9], the RPE has been used less commonly than the dropping mercury electrode (DME). Some rapid halogenations have been studied by Rao et al using the RPE[10]. Halogenations reactions in aqueous medium are generally of the second order so their half-lives can be extended by diluting the solutions. Convenient kinetic measurements can be carried out using the RPE.
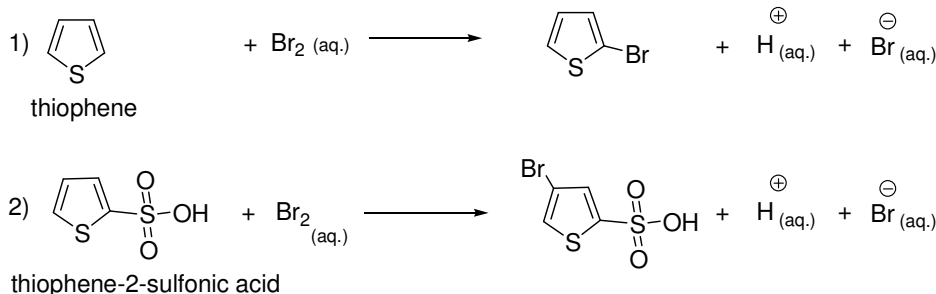
The product of second reaction is 4-bromo thiophene-2-sulfonic acid. It has been ascertained stoichiometrically and by nmr studies in both the reactions. In both the reactions, only Br_2 is electro-reducible at the RPE versus SCE and its concentration decreases with the reaction proceeds, is followed in terms I_D in nano-ampere.

Material and Methods

Chemicals: Stock solutions 0.001 M bromine, thiophene and thiophene-2-sulfonic acid were prepared in distilled water. Hundred fold, 0.1 M potassium nitrate was prepared as the supporting electrolyte. NaH_2PO_4 and Na_2HPO_4 each 0.5 M is prepared for the buffer system. The exact strength of the bromine solution stock solution has been determined by iodometric titration. Required concentration of reactants was prepared from stock solution.

RPE: RPE consists of an inverted 'T' shaped glass tube thirty centimeter long and half centimeter diameter, containing mercury. One centimeter of a platinum wire is fused at the tip of this glass tube of which half centimeter protrudes out. A copper wire is dipped in the glass tube for electric contact. The electrode assembly is mounted on a pair of pulleys and rotated at six hundred revolutions per minute by a synchronous motor. The inverted 'T' shape of the electrode facilitates stirring of the reaction mixture while rotating.

SCE: It is the reference electrode which is connected to negative end of battery.

Calibration of diffusion current: The SCE and RPE was dipped in fifty cm^3 of 0.02M KNO_3, the supporting electrolyte with required buffer solutions. A potential of + 0.1 V versus the SCE was applied at the RPE with the help of potentiometric arrangement. The galvanometer light spot was arranged to show zero deflection on the scale. KNO_3 solution was then replaced by fifty cm^3 of 0.0002M Br_2 solution containing 0.02M KNO_3 with the buffer component (table-2) which is maintaining seven pH. The specific shunt was selected to maintain spot within scale limit. One centimeter galvanometer light spot deflection on the scale corresponds to a diffusion current value of one nano-ampere. The shunt value was kept constant in the

experiment. All the readings are observed only after the solutions had attained the thermostat temperatures. The readings of calibration have been given in table-1 and in figure-1 at various temperatures.

Kinetic measurements: The reactants, thiophene-2-sulfonic acid and bromine undergo double dilution after mixing to a total volume of fifty cm^3. Hence, additions of the reactants are made as follow. 25 cm^3 of 0.000 4 M thiophene-2-sulphonic acid containing 0.02M KNO_3 with the required buffer components was kept in a flask in a thermostat maintained at the desired temperature. In another flask, 25 cm^3 of 0.0004M bromine containing 0.02M KNO_3 with the required buffer components were kept in the same thermostat. After the thermostat temperature was attained by all the solutions, the two reactant solutions were simultaneously added to the reaction vessel, kept in the thermostat, in which the SCE dipped and RPE was rotating. The unreacted bromine was recorded at every 10 seconds in terms of the galvanometer light spot on the scale. From the calibration plot at the relevant temperature, the unreacted concentration of Br_2 at various instants of time was evaluated in the kinetic run. The readings of kinetic measurements have been given in table-2 and in figure-2 for the temperature 24.5^0C

Determination of the energy of activation for the reactions : These quantitative studies are carried out at five different temperatures. From that quantitative data the thermodynamic parameters viz. the pre-exponential factor A, the entropy change ΔS and the energy of activation, E_a, for the reactions are evaluated.

Table–1
Calibration

[Br$_2$] / 10^{-4}M	Mean diffusion current/ nA				
	10.2^0C	12.0^0C	16.1^0C	20.2^0C	24.5^0C
0.4	7.5	7.9	8.1	8.5	9.0
0.8	15.0	15.5	16.2	17.0	17.0
1.2	22.5	23.2	24.5	25.8	26.5
1.6	30.0	31.0	32.7	33.9	35.5
2.0	38.0	38.9	41.1	43.0	44.7

Table–2
Kinetic readings of uncatalysed bromination of thiophene-2-sulfonic acid by bromine at 24.5^0c in aqueous medium at seven pH

Time/s	Diffusion current/ nA				[Br$_2$]/10^{-4}M	[Br$_2$]$^{-1}$/10^4 M^{-1}
	1	2	3	Mean		
20	31.7	31.70	31.7	31.7	1.41	0.71
30	26.9	27.10	27.0	27.0	1.23	0.82
40	24.2	24.00	24.1	24.0	1.09	0.92
50	22.0	22.10	22.0	22.0	0.97	1.03
60	19.7	19.70	19.7	19.7	0.88	1.14
70	18.0	17.90	18.1	18.0	0.80	1.25

Table - 3
Variation of specific reaction rate, k of uncatalysed bromination of thiophene-2-sulfonic acid by Br$_2$ at various temperatures in aqueous medium at seven pH

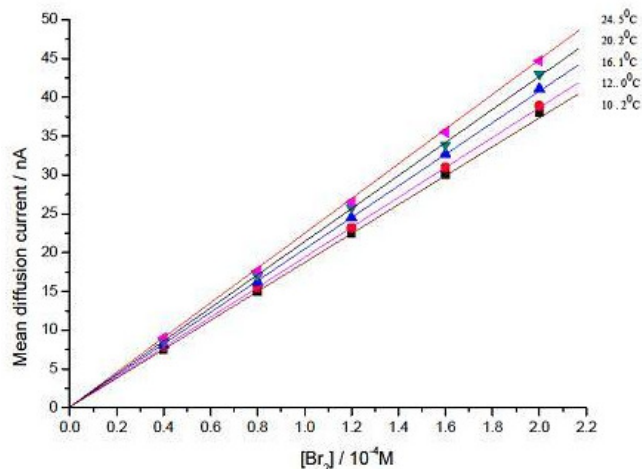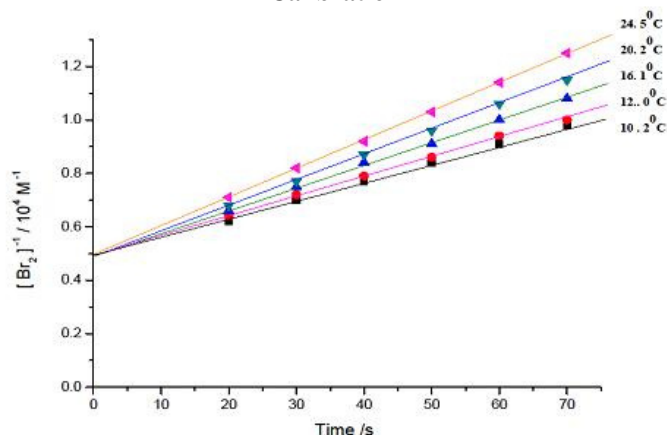| Temperature/ K	[T] $^{-1}$/ 10^{-3} K^{-1}	k/ M^{-1}s^{-1}	log k
283.20	3.53	41.00	1.55
285.00	3.51	45.70	1.66
289.10	3.46	55.00	1.74
293.20	3.41	83.30	1.92
297.50	3.36	106.00	2.03

Figure-1
Calibration

Figure - 2
Kinetics of uncatalysed bromination of thiophene-2-sulfonic acid by bromine at various temperatures in aqueous medium at 7 pH

Results and Discussion

The plot of [Br$_2$]$^{-1}$ Vs time, t is a straight line at all temperatures for both the reactions, hence both the reactions follow second order kinetics and the slopes of these lines indicate the specific reaction rates (k) are as shown in the table-3
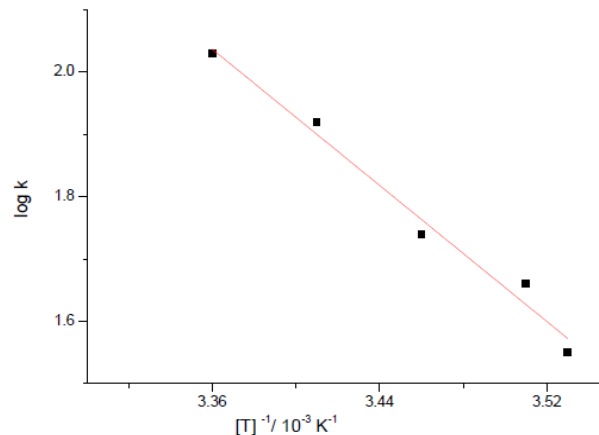

Figure–3
Arrhenius plot

The specific reaction rate, k of the bromination of thiophene in aqueous solution at 7 pH is found to be 526.5 M^{-1}s^{-1} at 24.5^{0}C. The energy of activation, Ea is evaluated to be 26.50 kJ mol^{-1}. The frequency factor 'A' is found to be 2.26 x 10^7 M^{-1}s^{-1} and the entropy change, ΔS for the reaction is found to be-112.15 J mol^{-1}K^{-1}.

The specific reaction rate, k of the bromination of thiophene-2-sulfonic acid in aqueous solution at 7 pH is found to be 106.0 M^{-1}s^{-1} at 24.5^{0}C. The energy of activation, Ea is evaluated to be 52.20 kJ mol^{-1}.The frequency factor, A is found to be 1.55 x 10^{11} M^{-1}s^{-1} and the entropy change, ΔS for the reaction is found to be -39.00 J mol^{-1}K^{-1} .

Accepted mechanism for electrophilic substitution reactions, the bromination of thiophene-2-sulfonic acid in aqueous solution by molecular bromine may be as follows.
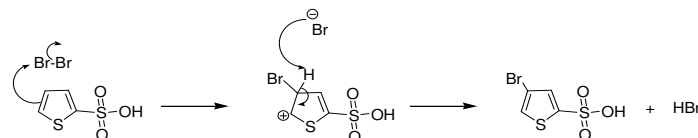
Bromine is known to hydrolyze in aqueous solutions according to the equilibrium

$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$$
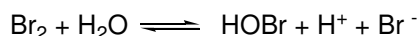
The forward and reverse specific rates of this hydrolysis equilibrium are 1.1 × 10^{2}s^{-1} and 10^{10} M^{-2}s^{-1} respectively[11]. Aromatic substrates are known to react very slowly with hypohalous acids as compared to molecular halogens; hence all the equilibrium concentration of HOBr is rapidly converted into the more reactive species, the bromine molecule, which may be considered to be the sole brominating species. The possibility of protonated H$_2$OBr$^+$ as the prime brominating species or a catalytic effect of H$^+$ on the halogenation is ruled out as the pH of the reaction is 7.

The lower specific reaction rate observed for the bromination of thiophene-2-sulfonic acid quantitatively confirms the substituent effect of the sulfonic group as follows in table-4.

Table - 4
A comparison of the kinetic and thermodynamic parameters for the bromination of thiophene and thiophene-2-sulfonic acid by bromine in aqueous solution at 24.5^{0}C

No.	Parameter	Thiophene	Thiophene-2-sulfonic acid
1	Initial reactant concentration / M	5×10^{-5}	2×10^{-4}
2	Specific reaction rate,k / $M^{-1}s^{-1}$	526.5	106.0
3	Half-life / s	38	46
4	Energy of activation, E_a / kJ mol^{-1}	26.5	52.2
5	Frequency factor, A / $M^{-1} s^{-1}$	2.26×10^7	1.55×10^{11}
6	Entropy change, ΔS / $JK^{-1}mol^{-1}$	-112.15	-39.00

Conclusion

The presence of the electron withdrawing sulfonic acid group in thiophene-2-sulfonic acid molecule reduces the nucleophilicity of the five member aromatic ring relative to that of the thiophene molecule. Hence the electrophilic attack of the positive end, due to the induced dipole in the bromine molecule is considerably hampered in the case of thiophene-2-sulfonic acid molecule relative to that in the case of thiophene molecule. This reduced reactivity for bromination of thiophene-2-sulfonic acid relative to thiophene is quantitatively established in this kinetic investigation. The lower reactivity is manifest from the higher energy of activation ,the greater value of the frequency factor and the lower negative value of the entropy change, all stemming from the relatively lower specific reaction rate for the bromination of the less nucleophilic thiophene sulfonic acid compared to the bromination of thiophene. Thus, the quantitative assertion of the relative speculated reactivities of the two aromatic substrates, thiophene and thiophene-2-sulfonic acid for uncatalyzed bromination at seven pH in aqueous medium is hereby obtained.

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